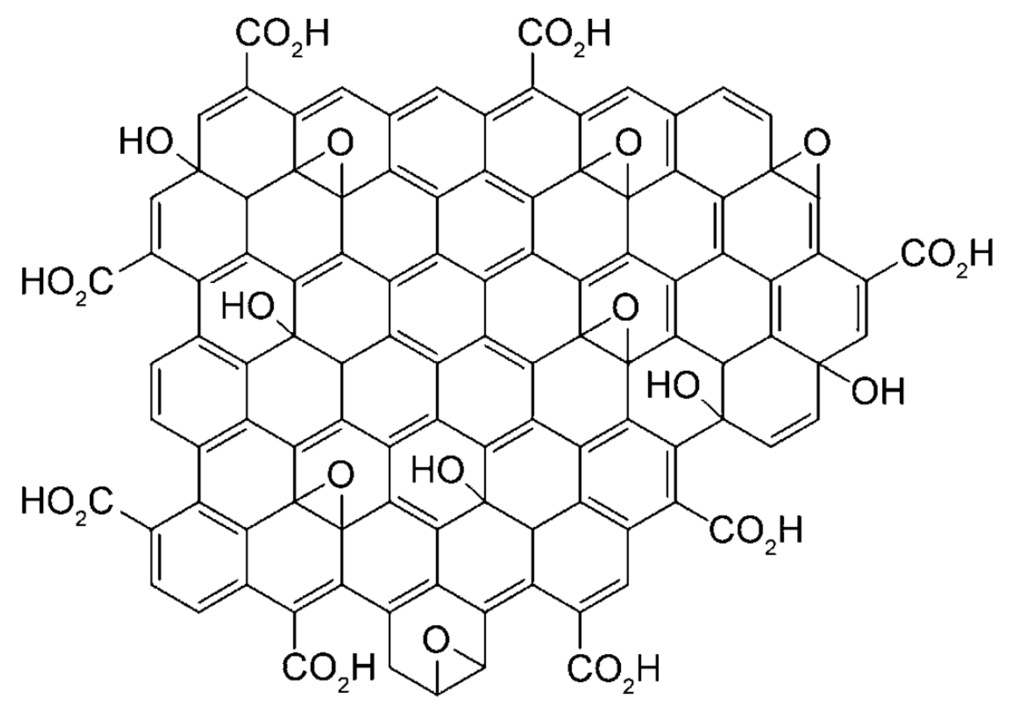
Photo-initiated grafting polymerization on graphene oxide

Hewen Liu

Department of Polymer Science and Engineering, University of Science and Technology of China, China.

Structure of graphene oxide (GO)



- A novel 2D carbonaceous nanomaterial
- Abundant functional groups, such as hydroxyls, epoxies, and carboxylic acids

Chemical Functionalization of GO

- Chemical Functionalization via surface groups:
  - Hydroxyls
  - Carboxylic acids
- Chemical Functionalization via free radical attachment.
- Chemical Functionalization via physical-chemical approaches

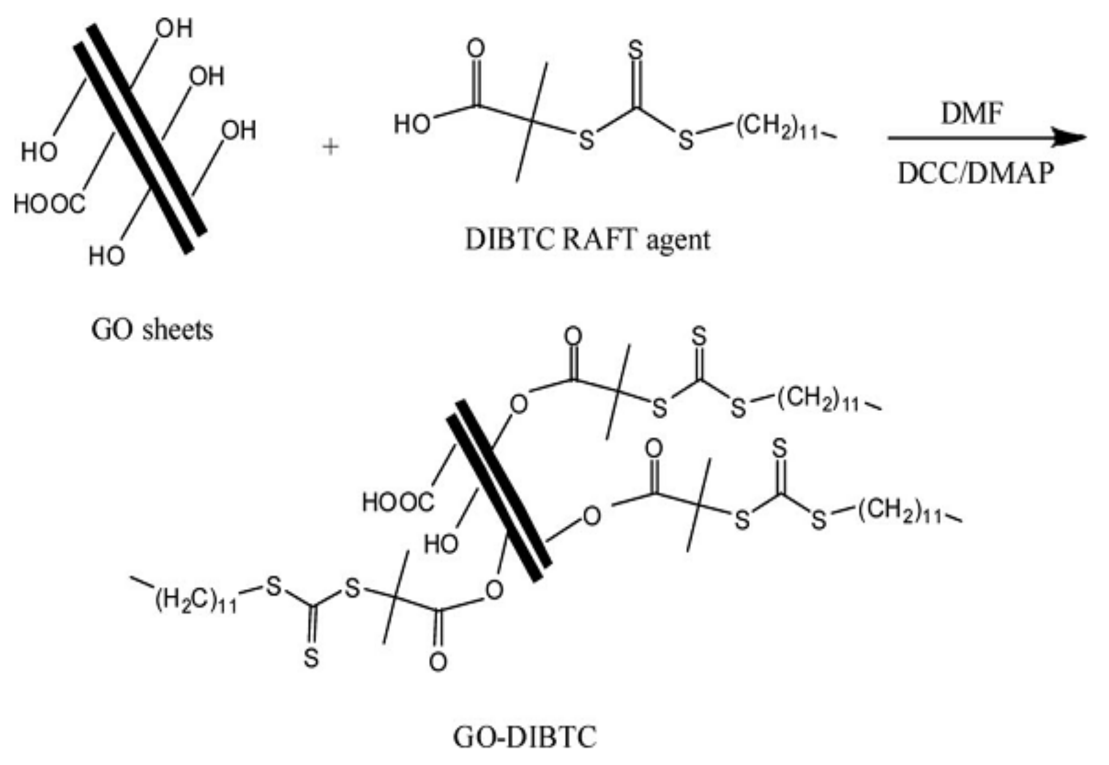
Chemical functionalization via surface hydroxyl groups

-OH

Starting groups for the attachment of free radical initiating sites of vinyl polymerization

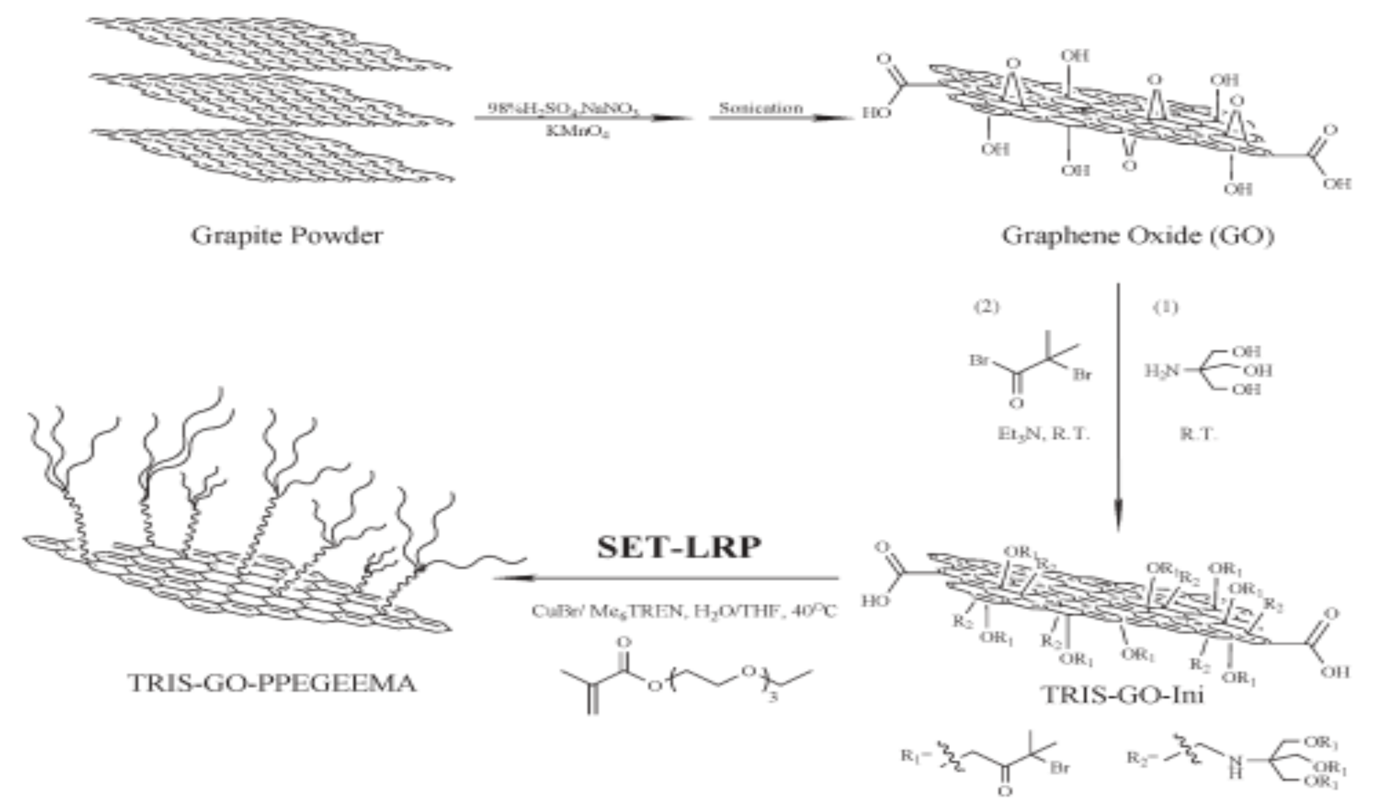
Initiating sites for step polymerization: ring-opening polymerization

Synthesis and Characterization of Polystyrene-Graphite Nanocomposites via Surface RAFT-Mediated Miniemulsion Polymerization



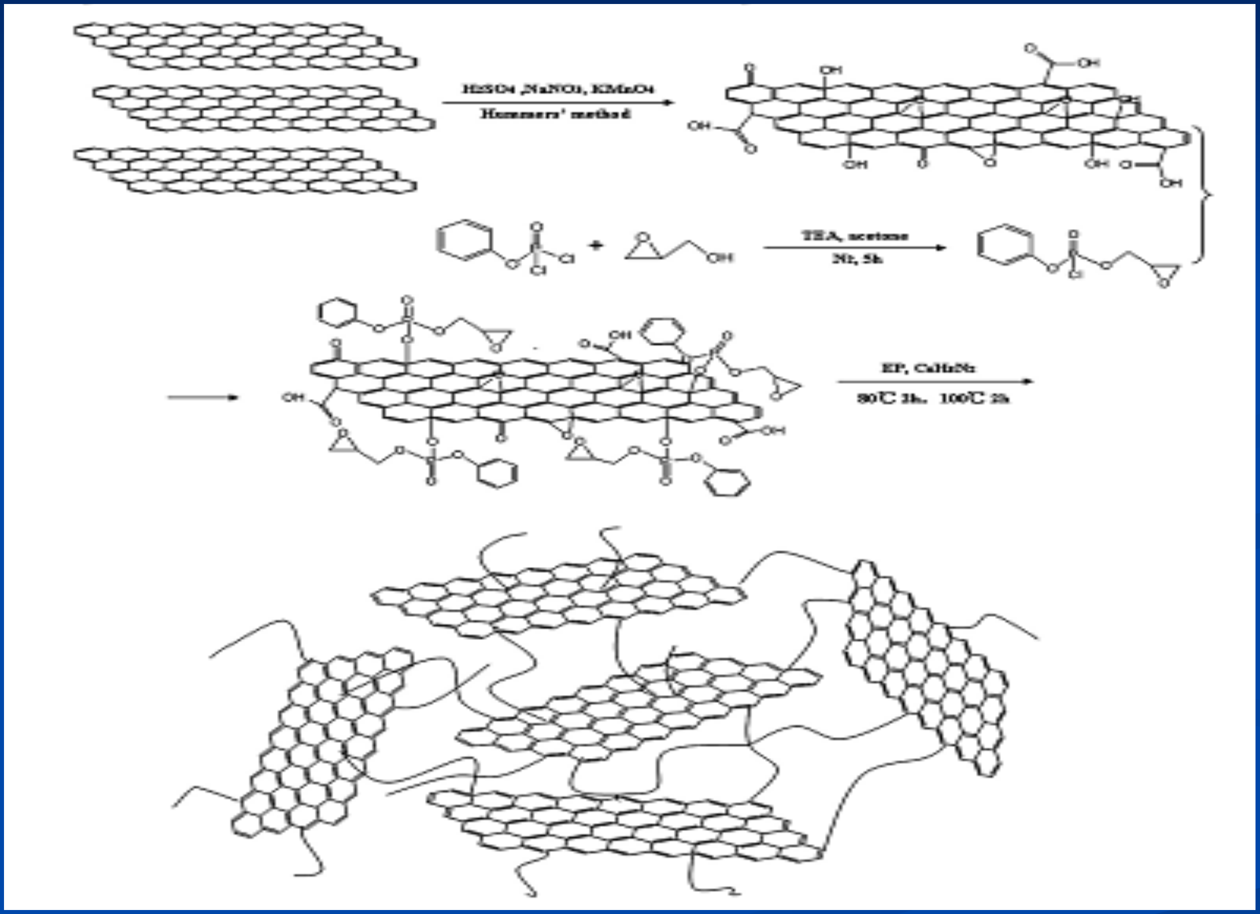
H. M. Etmimi,,M. P. Tonge,R. D. Sanderson
J. Polym. Sci. Part A: Polym. Chem. 2011, 49, 1621–1632.

Functionalization of Graphene Oxide Towards Thermo-Sensitive Nanocomposites via Moderate In Situ SET-LRP



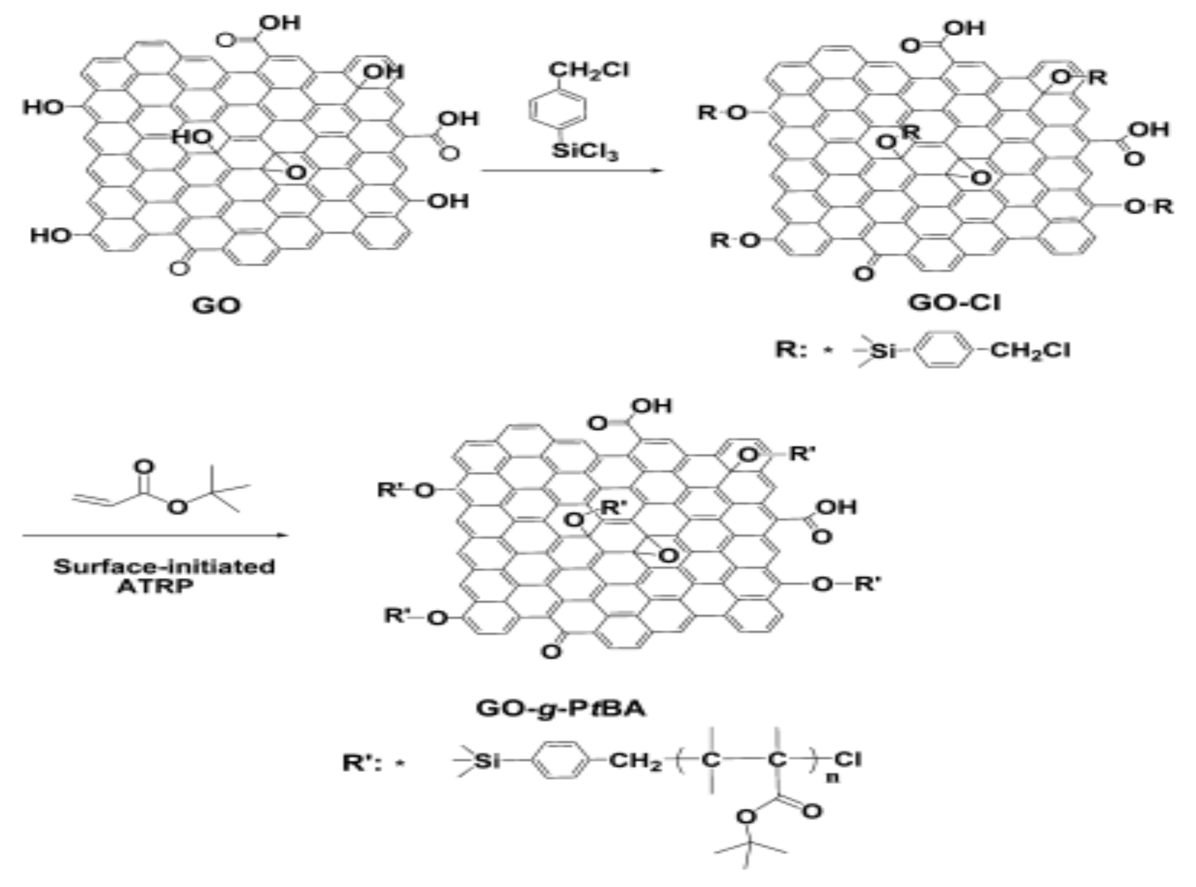
Yan D eng,Yongjun Li,Jing Dai,Meidong Lang,Xiaoyu Huang
J. Polym. Sci. Part A: Polym. Chem. 2011, 49, 4747–4755

In Situ Polymerization of Graphene, Graphite Oxide, and Functionalized Graphite Oxide into Epoxy Resin and Comparison Study of On-the-Flame Behavior



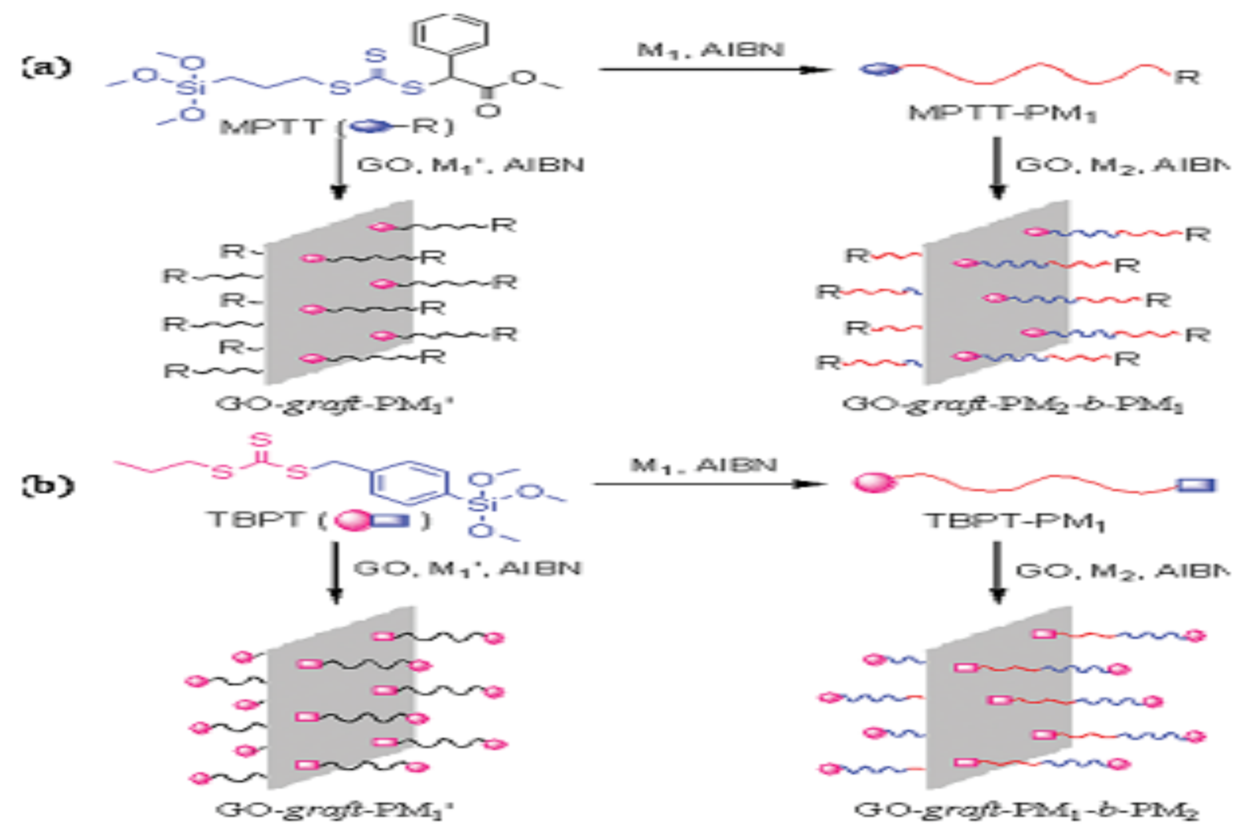
Yuqiang Guo, Chenlu Bao, Lei Song, Bihe Yuan, and Yuan Hu
Ind. Eng. Chem. Res. 2011, 50, 7772–7783

Organo- and Water-Dispersible Graphene Oxide-Polymer Nanosheets for Organic Electronic Memory and Gold Nanocomposites



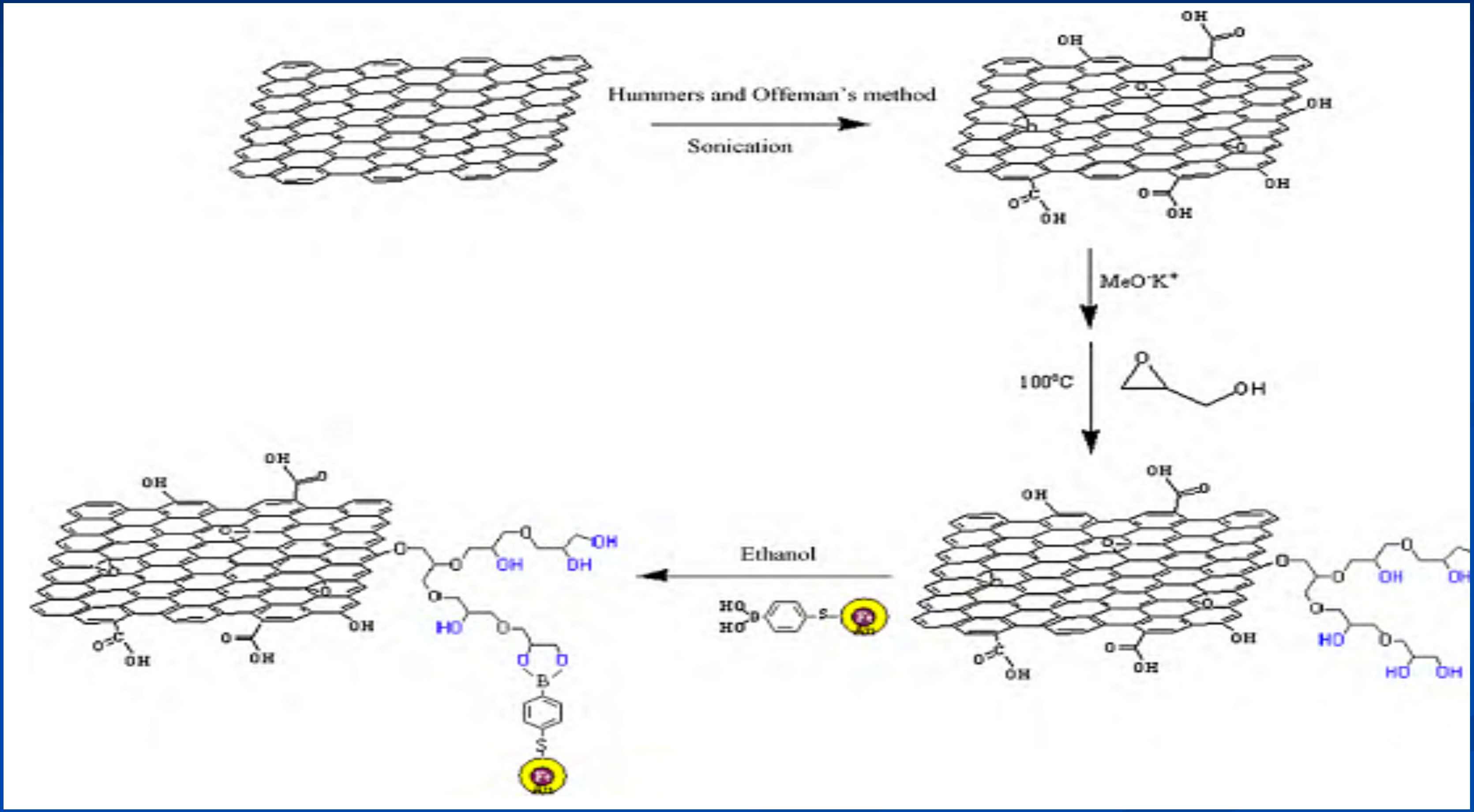
Guo Liang Li, Gang Liu, Min Li, Dong Wan, K. G. Neoh, and E. T. Kang
J. Phys. Chem. C, Vol. 114, No. 29, 2010

One-Pot Controlled Synthesis of Homopolymers and Diblock Copolymers Grafted Graphene Oxide Using Couplable RAFT Agents



Kun Jiang, Chunnuan Ye, Peipei Zhang, Xiaosong Wang,and Youliang Zhao
Macromolecules 2012, 45, 1346– 1355

Covalent functionalization of graphene oxide with polyglycerol and their use as templates for anchoring magnetic nanoparticles

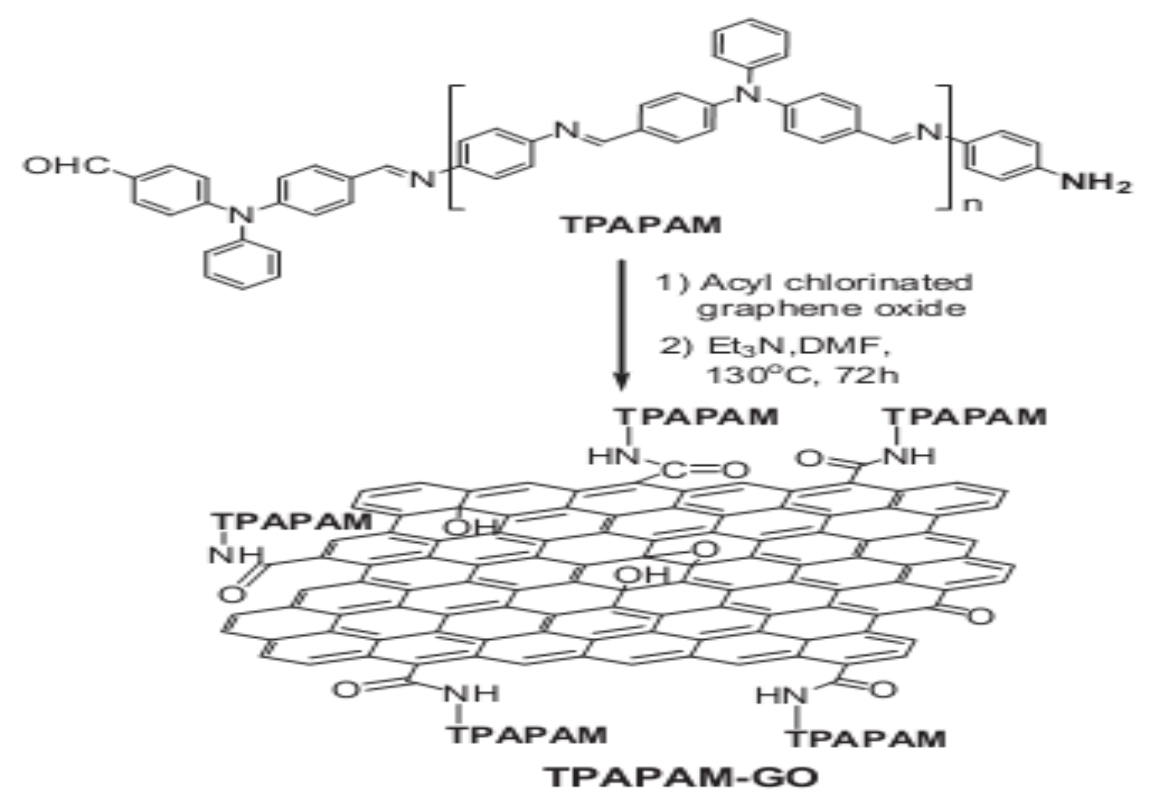


Tuan Anh Pham, Nanjundan Ashok Kumar, Yeon Tae Jeong
Synthetic Metals, 2010, 160, 2028–2036.

Chemical functionalization via surface carboxylic groups

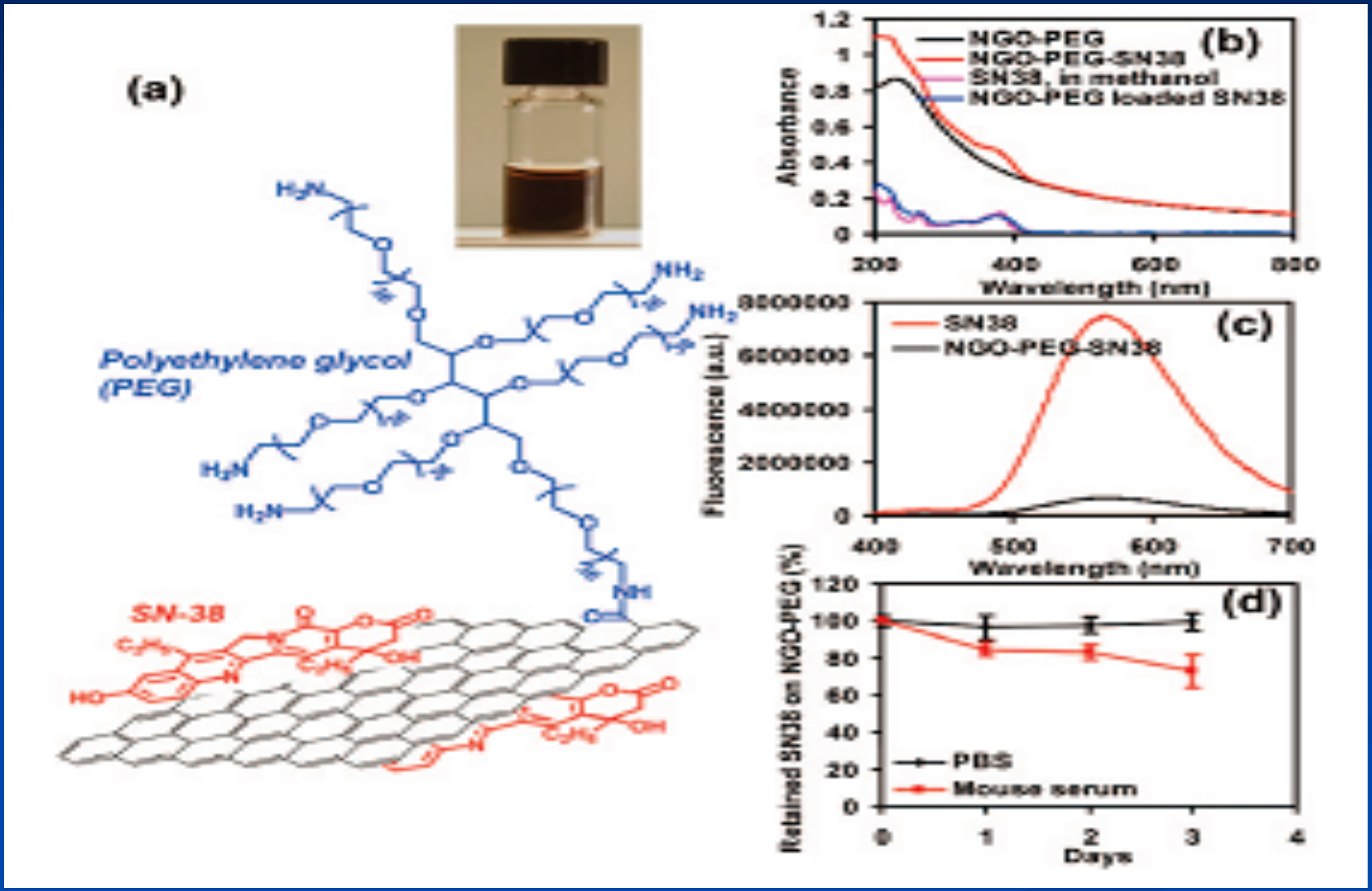
-COOH
Amidation reaction

Conjugated- Polymer-Functionalized Graphene Oxide: Synthesis and Nonvolatile Rewritable Memory Effect



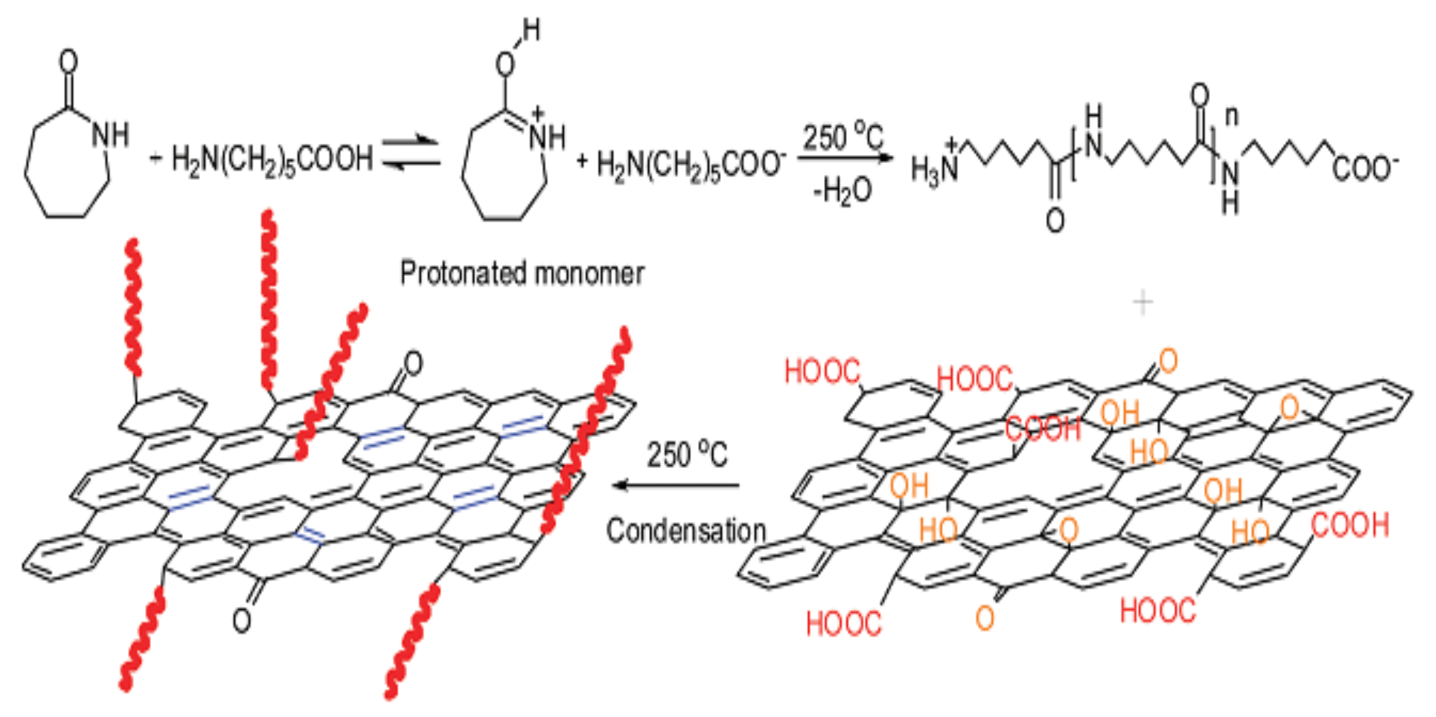
Xiao-Dong Zhuang, Yu Chen, Gang Liu, Pei-Pei Li, Chun-Xiang Zhu,
En-Tang Kang, Koon-Gee Neoh, Bin Zhang, Jin-Hui Zhu, and Yong-Xi Li
Adv. Mater. 2010, 22, 1731–1735

PEGylated Nanographene Oxide for Delivery of Water-Insoluble Cancer Drugs



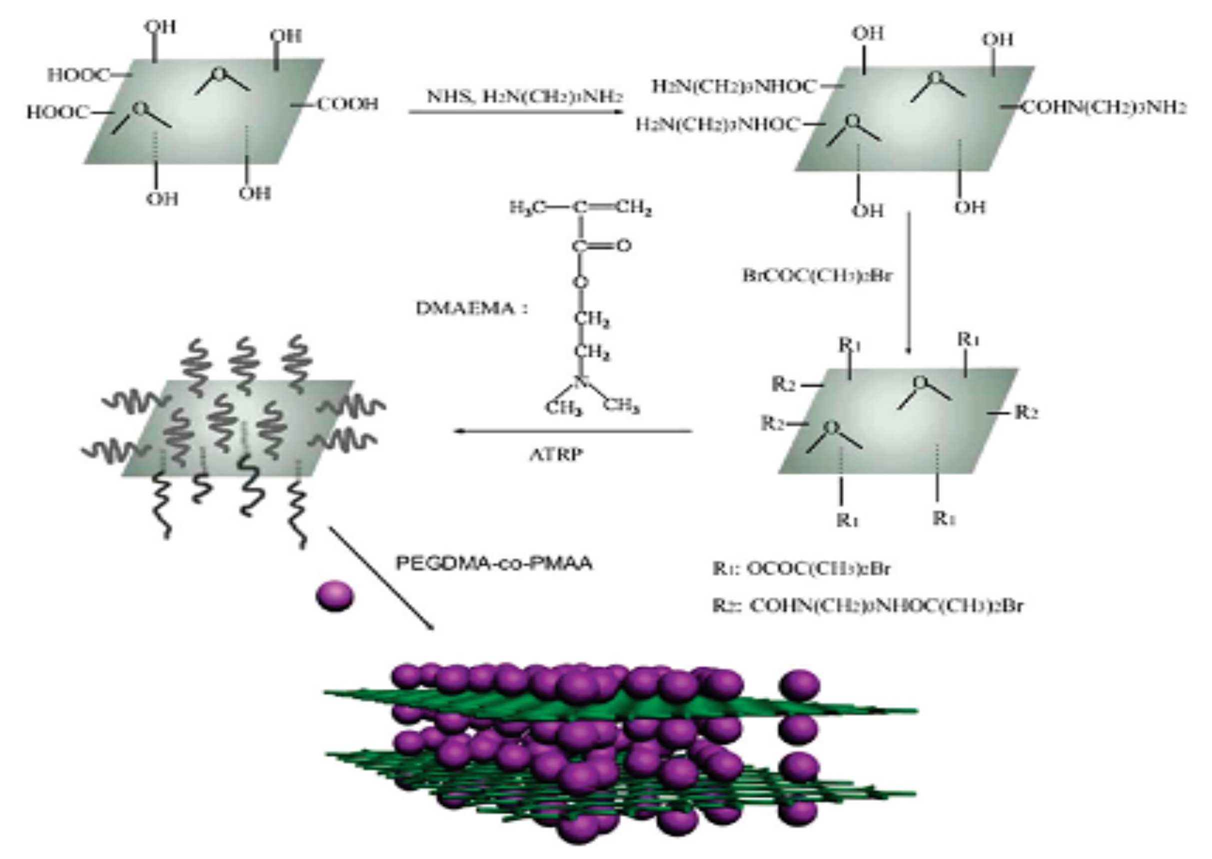
Zhuang Liu, Joshua T. Robinson, Xiaoming Sun, and Hongjie Dai
J. Am. Chem. Soc. 2008 , 130 , 10876–10877.

In situ Polymerization Approach to Graphene-Reinforced Nylon-6 Composites



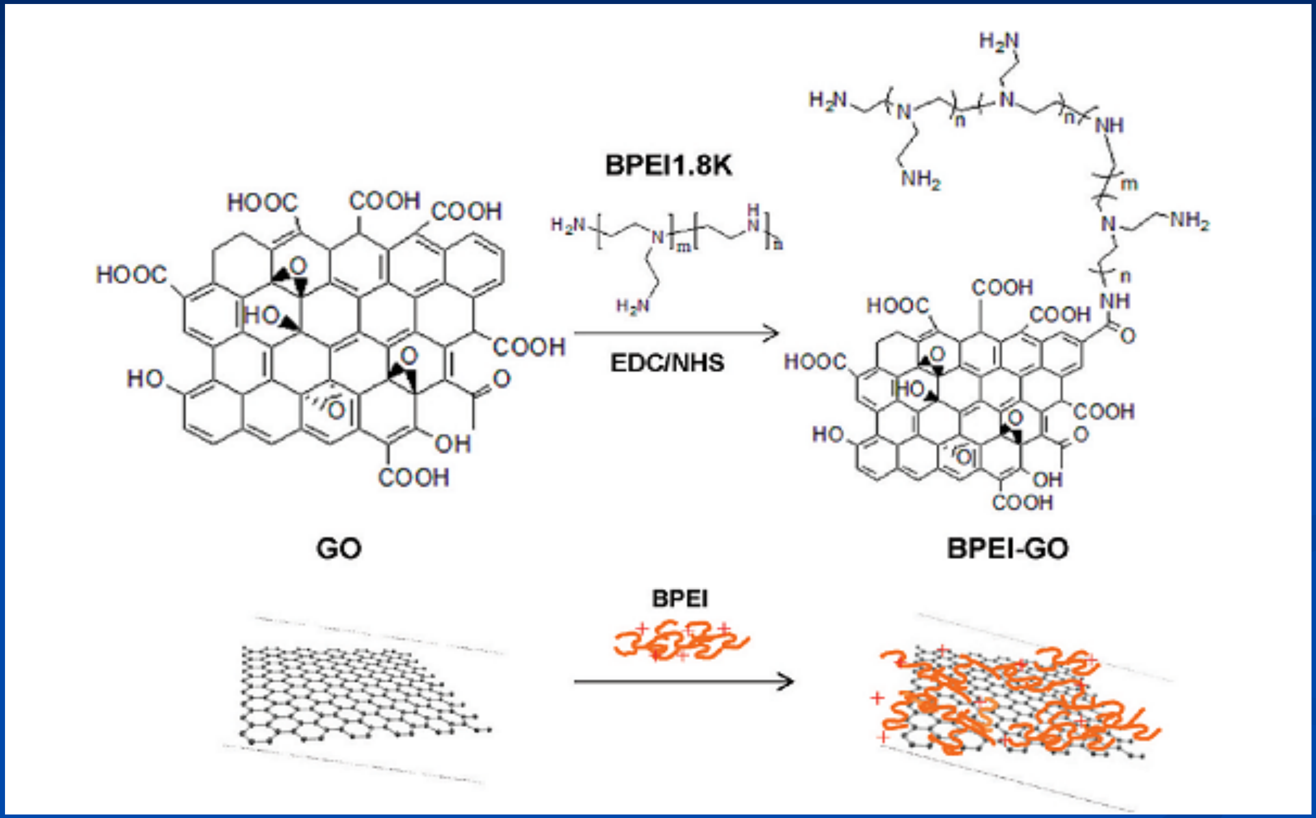
Zhen Xu and Chao Gao
Macromolecules, 2010, 43, 6716–6723

Exfoliated Graphite Oxide Decorated by PDMAEMA Chains and Polymer Particles



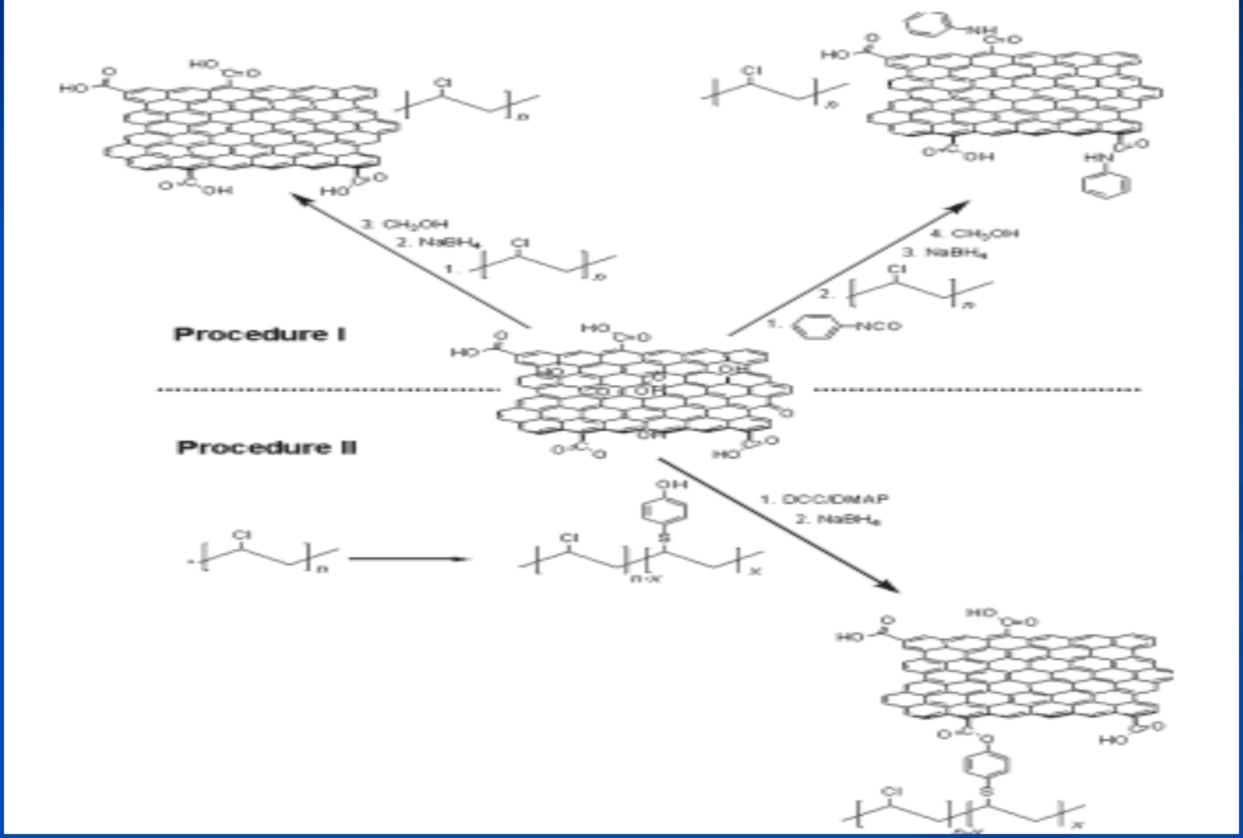
Yongfang Yang, Jie Wang,Jian Zhang, Jinchuan Liu, Xinglin Yang,
Hanying Zhao
Langmuir2009, 25, 11808–11814.

Graphene Oxide–Polyethylenimine Nanoconstruct as a Gene Delivery Vector and Bioimaging Tool



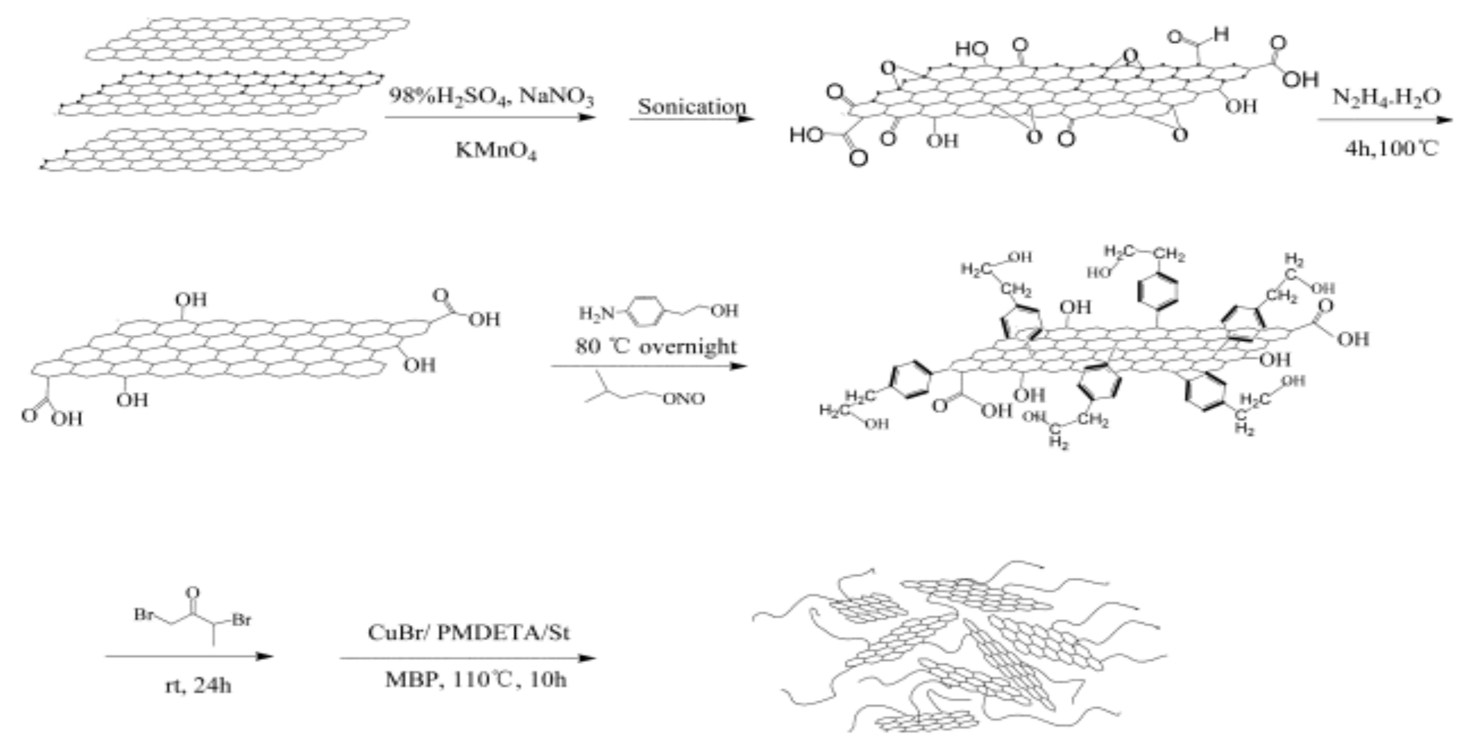
Hyunwoo Kim,Ran Namgung,Kaushik Singha,Il-Kwon Oh, Won Jong Kim
Bioconjugate Chem.2011, 22, 2558–2567.

Importance of Covalent Linkages in the Preparation of Effective Reduced Graphene OxidePoly(vinyl chloride) Nanocomposites



Horacio J. Salavagione, Gerardo Martínez
Macromolecules 2011, 44, 2685–2692

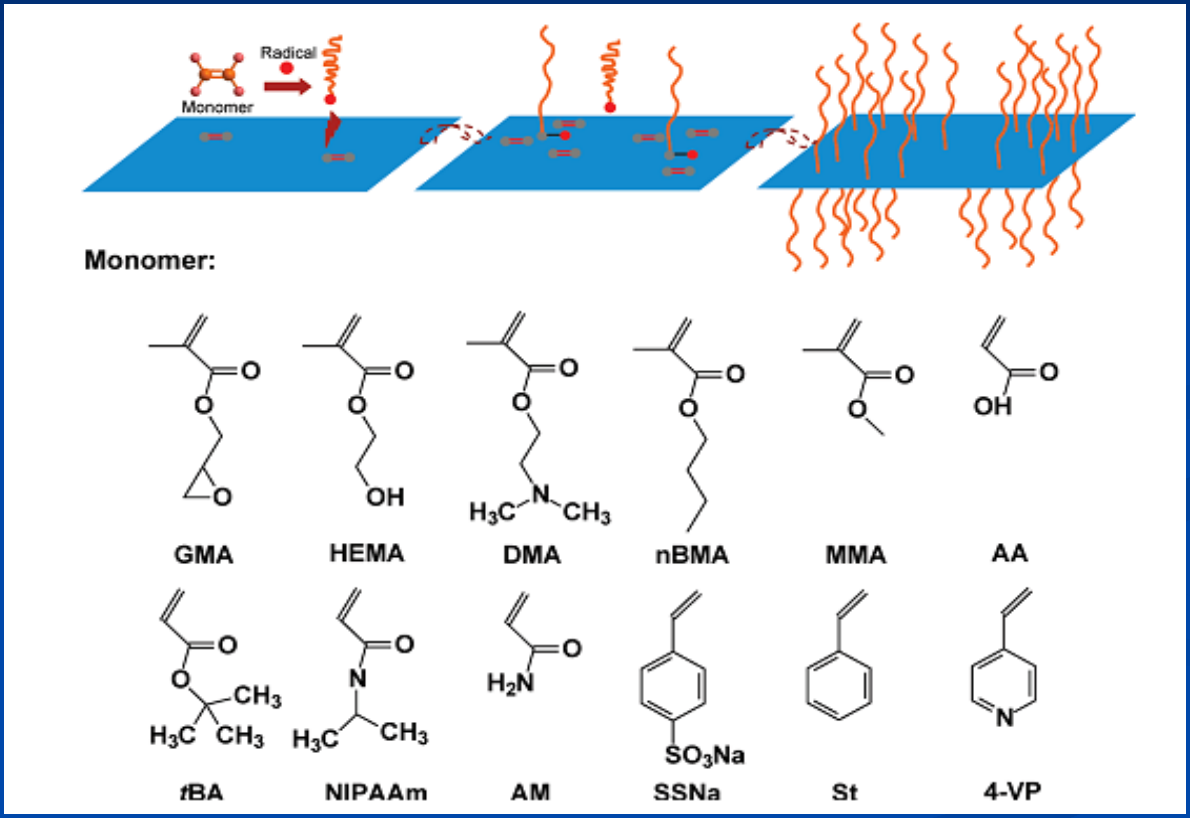
Covalent polymer functionalization of graphene nanosheets and mechanical properties of composites



Ming Fang,Kaigang Wang,Hongbin Lu,Yuliang Yangand Steven Nutt
J. Mater. Chem. , 2009, 19, 7098–7105.

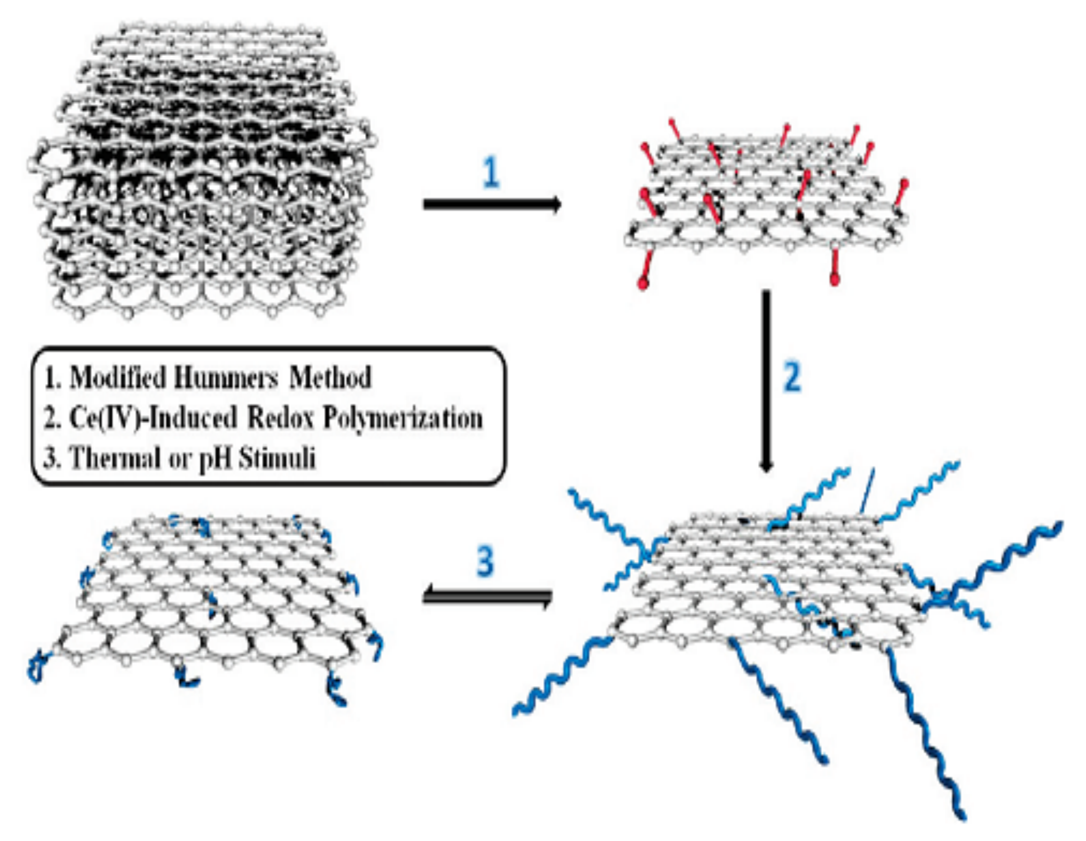
Chemical Functionalization via free radical attachment

General Avenue to Individually Dispersed Graphene Oxide-Based Two-Dimensional Molecular Brushes by Free Radical Polymerization



Lanyan Kan, Zhen Xu, Chao Gao
Macromolecules 2011, 44, 444–452

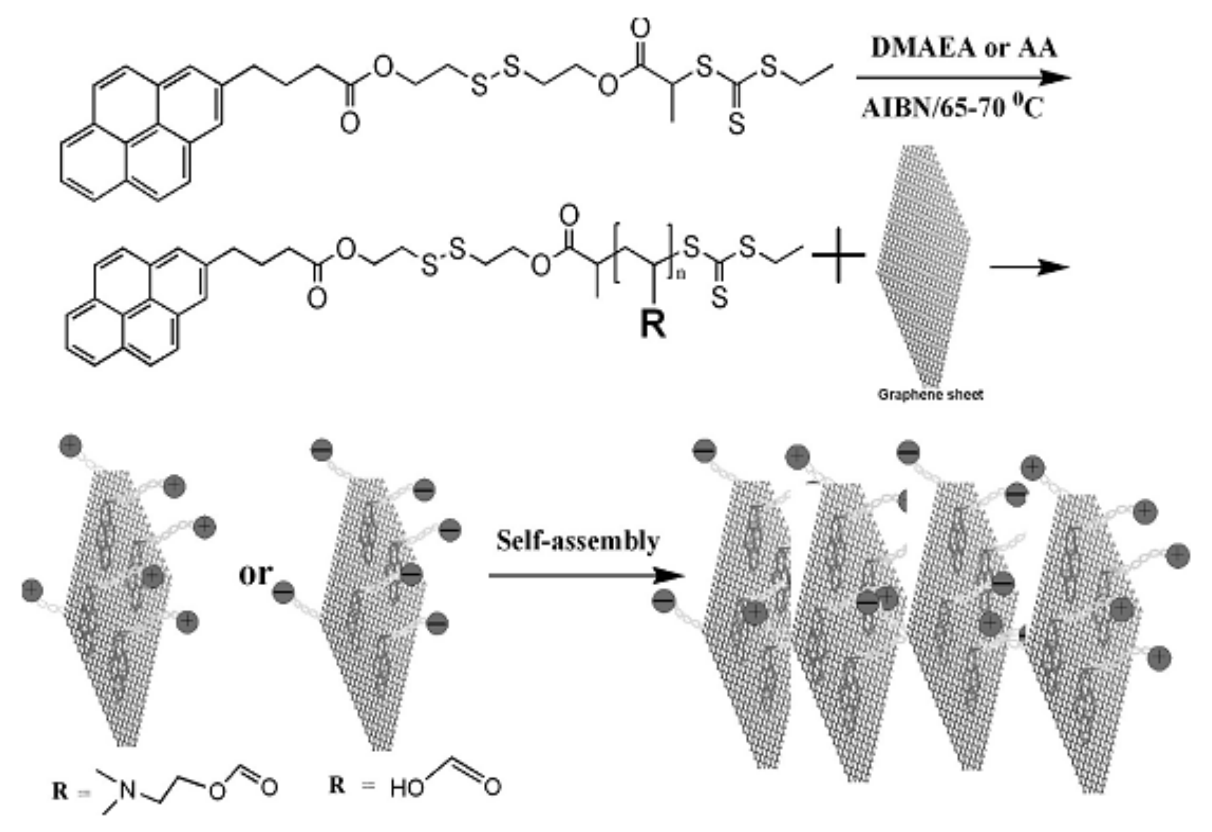
Stimuli-Responsive Polymer Covalent Functionalization of Graphene Oxide by Ce(IV)-Induced Redox Polymerization



Beidi Wang,Dong Yang, Jin Zhong Zhang, Chenbin Xi, Jianhua Hu
J. Phys. Chem. C 2011, 115, 24636–24641

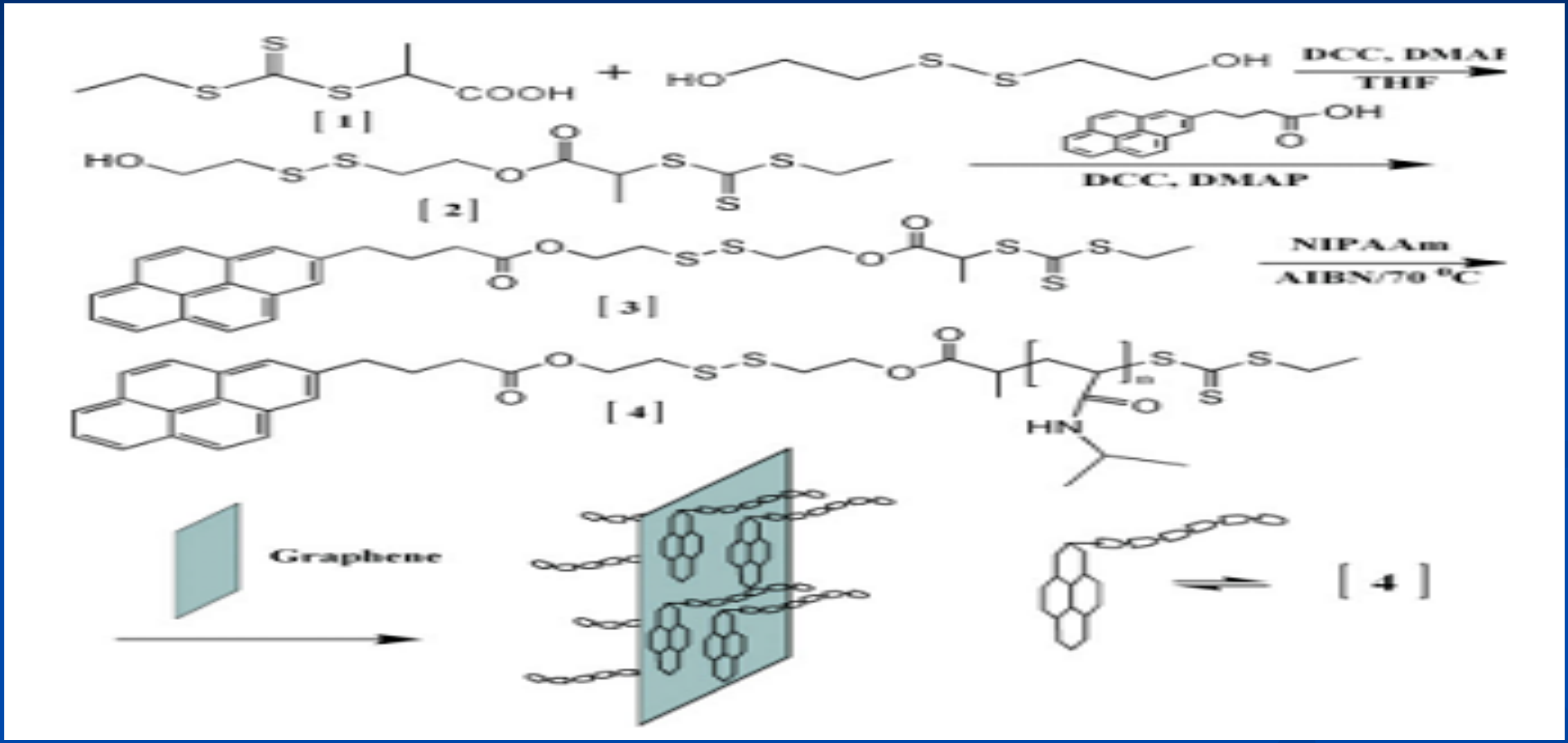
Chemical Functionalization via π –π stacking

Synthesis, Characterization, and Multilayer Assembly of pH Sensitive Graphene- Polymer Nanocomposites



Jingquan Liu,Lei Tao,Wenrong Yang,Dan Li,Cyrille Boyer,Richard Wuhrer,Filip Braet, Thomas P. Davis
Langmuir, 2010, 26 , 10068–10075.

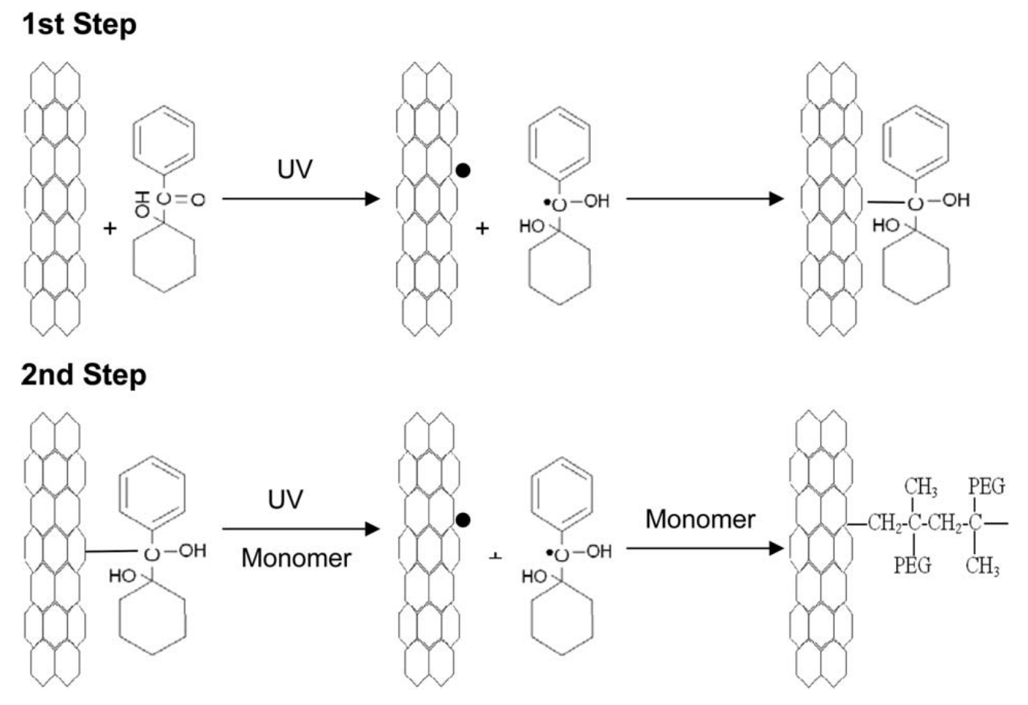
Thermosensitive Graphene Nanocomposites Formed Using Pyrene-Terminal Polymers Made by RAFT Polymerization



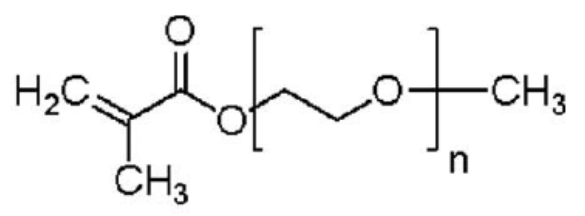
Jingquan Liu, Wenrong Yang, Lei Tao, Dan Li, Cyrille Boyer, Thomas P. Davis
J. Polym. Sci. Part A: Polym. Chem.
2010, 48, 425–433.

Photoinitiated graft onto carbonaceous materials

Synthesis of PEGylated Single Wall Carbon Nanotubes by a Photoinitiated Graft From Polymerization

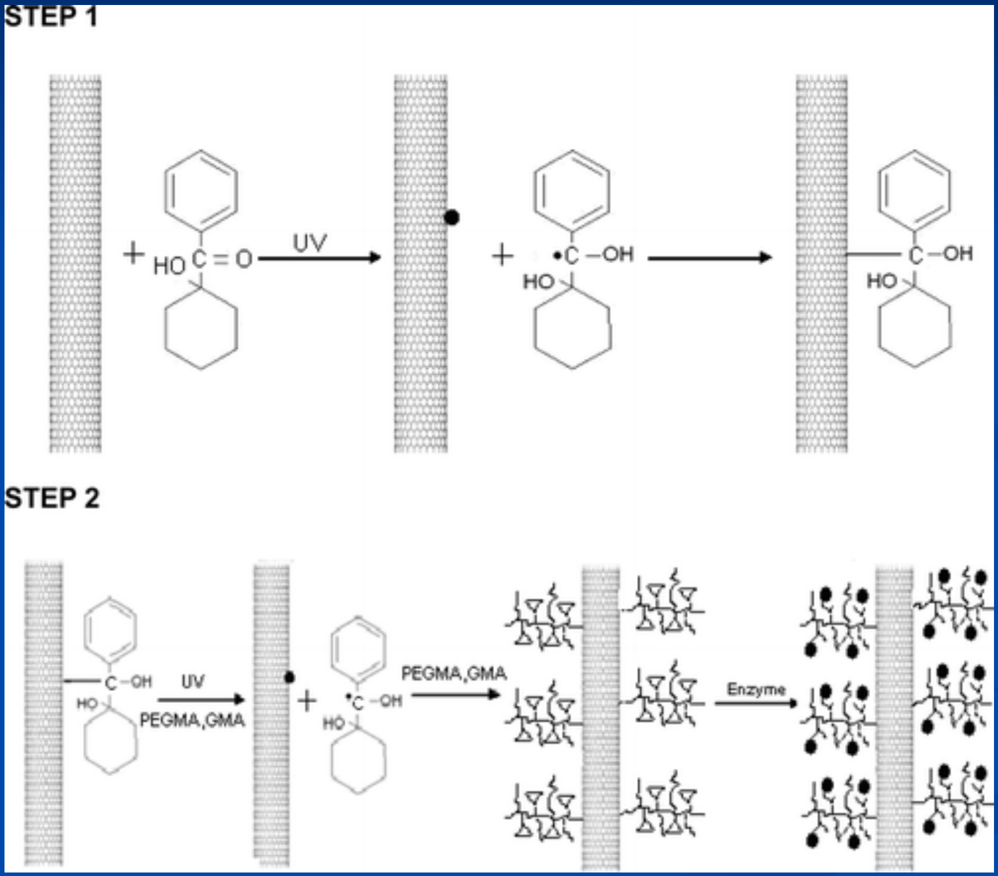


monomer



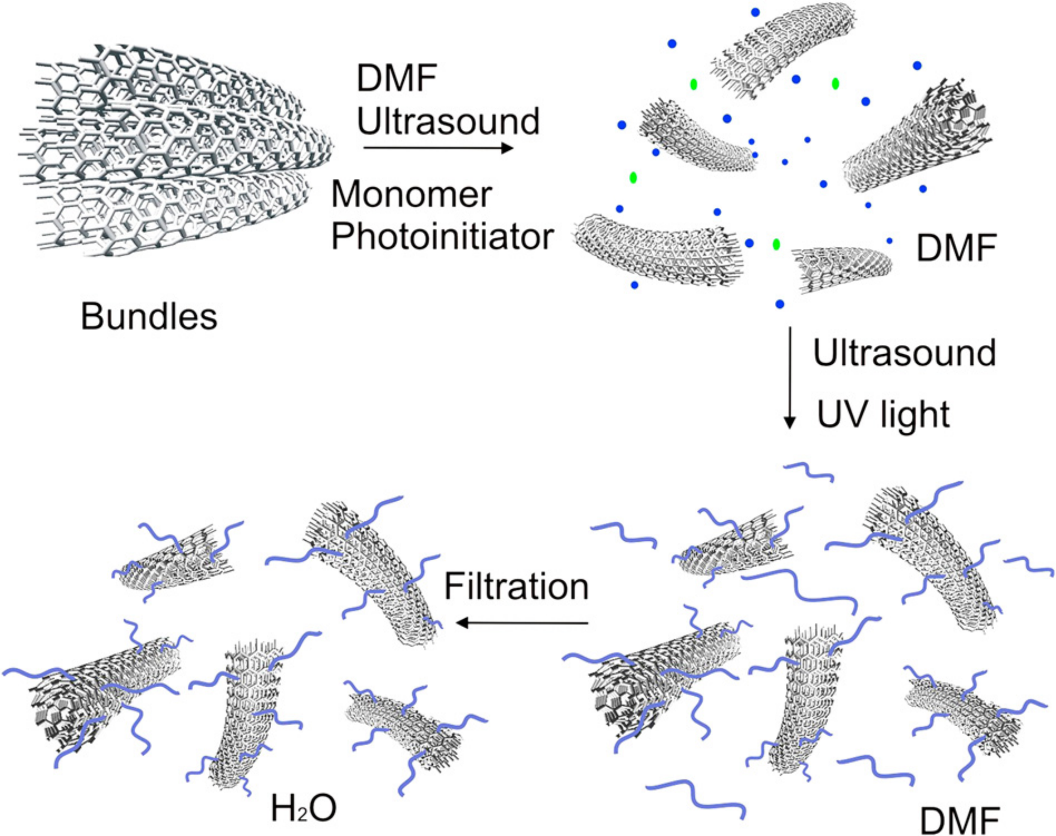
Pu Zhang and David B. Henthorn AIChE, 2010, 56, 1610-1615.

Fabrication of High-Capacity Biomolecular Carriers from Dispersible Single-Walled Carbon Nanotube–Polymer Composites



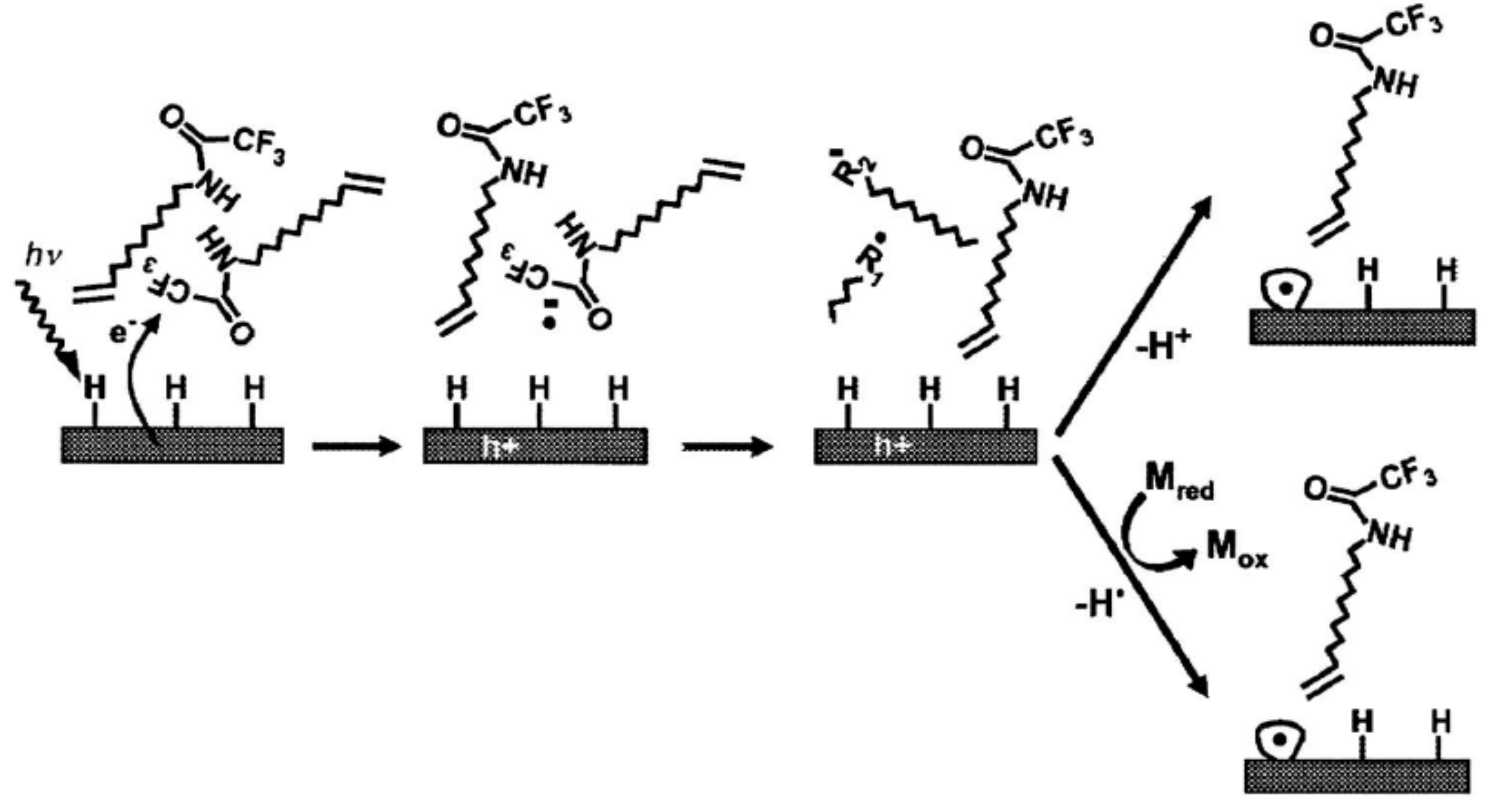
Pu Zhang and David B. Henthorn
Langmuir, 2009, 25, 12308–12314

UV-assisted grafting of polymers to multi-walled carbon nanotubes



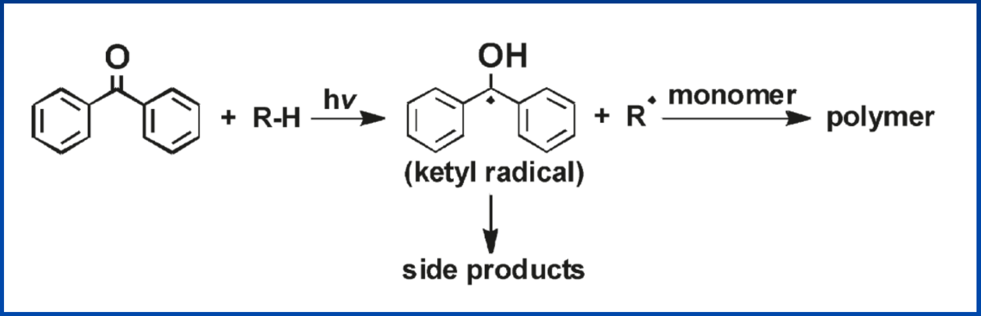
Petar Petrov, Georgi Georgiev, Denica Momekova, Georgi Momekov, Christo B. Tsvetanov
Polymer 2010, 51, 2465-2471.

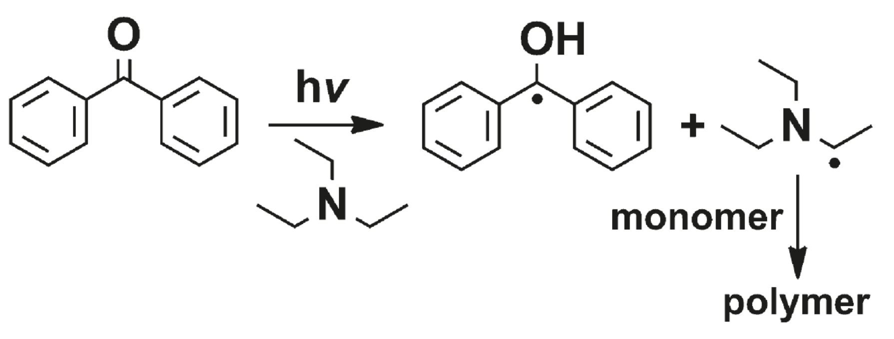
Photo-induced surface functionalization of carbon surfaces: The role of photoelectron ejection



Paula E. Colavita, Bin Sun, Kiu-Yuen Tse, Robert J. Hamers
J. Vac. Sci. Technol. 2008, A 26, 925-931.

Photoinitiators





Photoinitiators for radical polymerization are classified as

- Cleavage (type I) initiators
- H-abstraction type (type II) initiators.

Photoinitiated graft onto graphene oxide

Work of initial phase

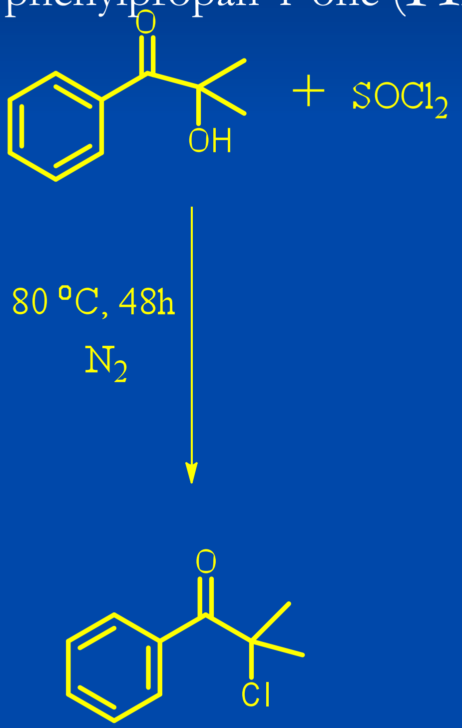
Experimental

- Chemical attachment of type II photoinitiators onto GO which initiate surface grafting polymerization.
- Or, Mixture of type II photoinitiators, monomers and GO are subject to UV exposure.
- Products were repeatedly purified by centrifugal separation at 10,000 g.

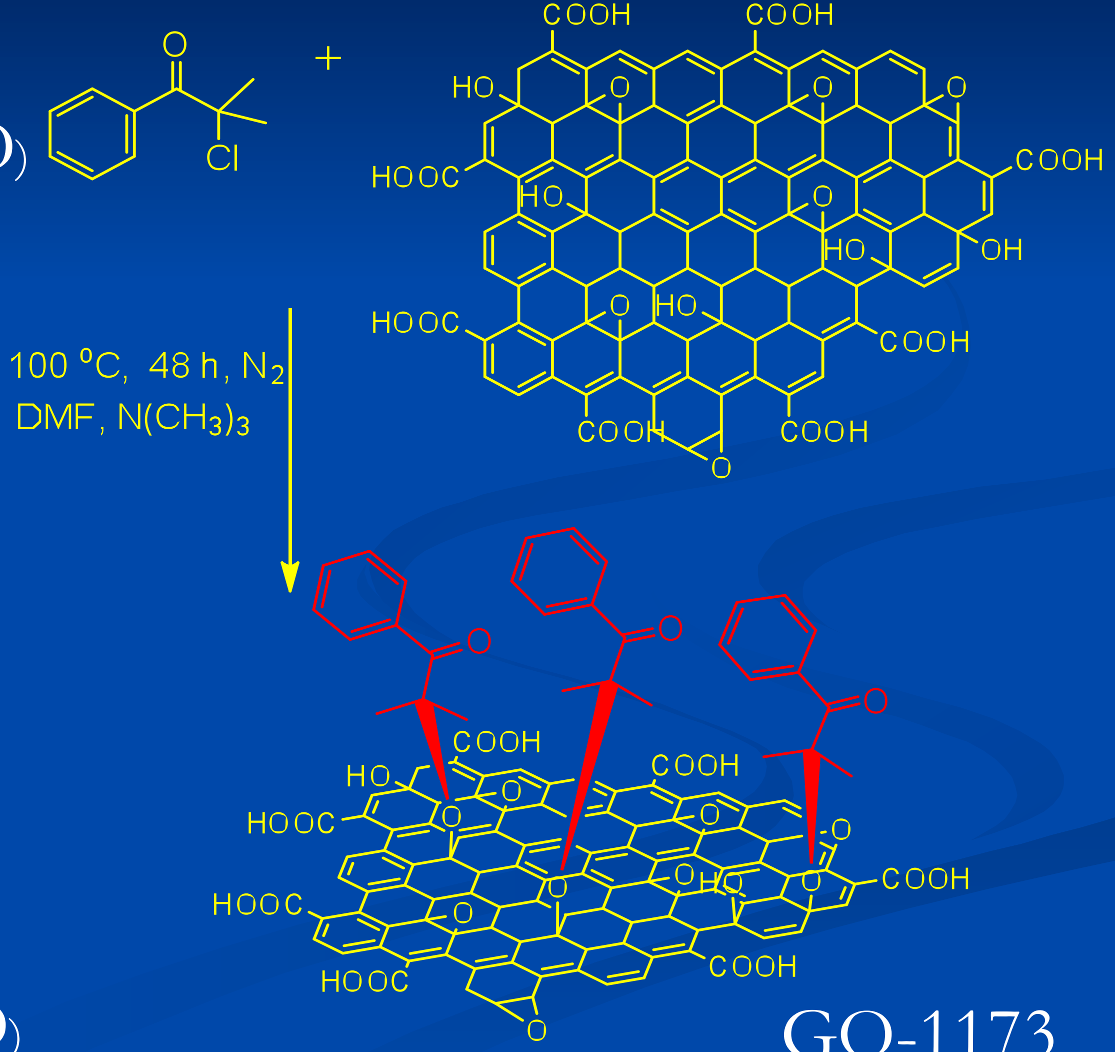
Photoinitiated graft of PDMAEMA via surface immobilized initiator

Chemical attachment of photoinitiator

2-hydroxy-2-methyl-
1-phenylpropan-1-one (HMPPO)

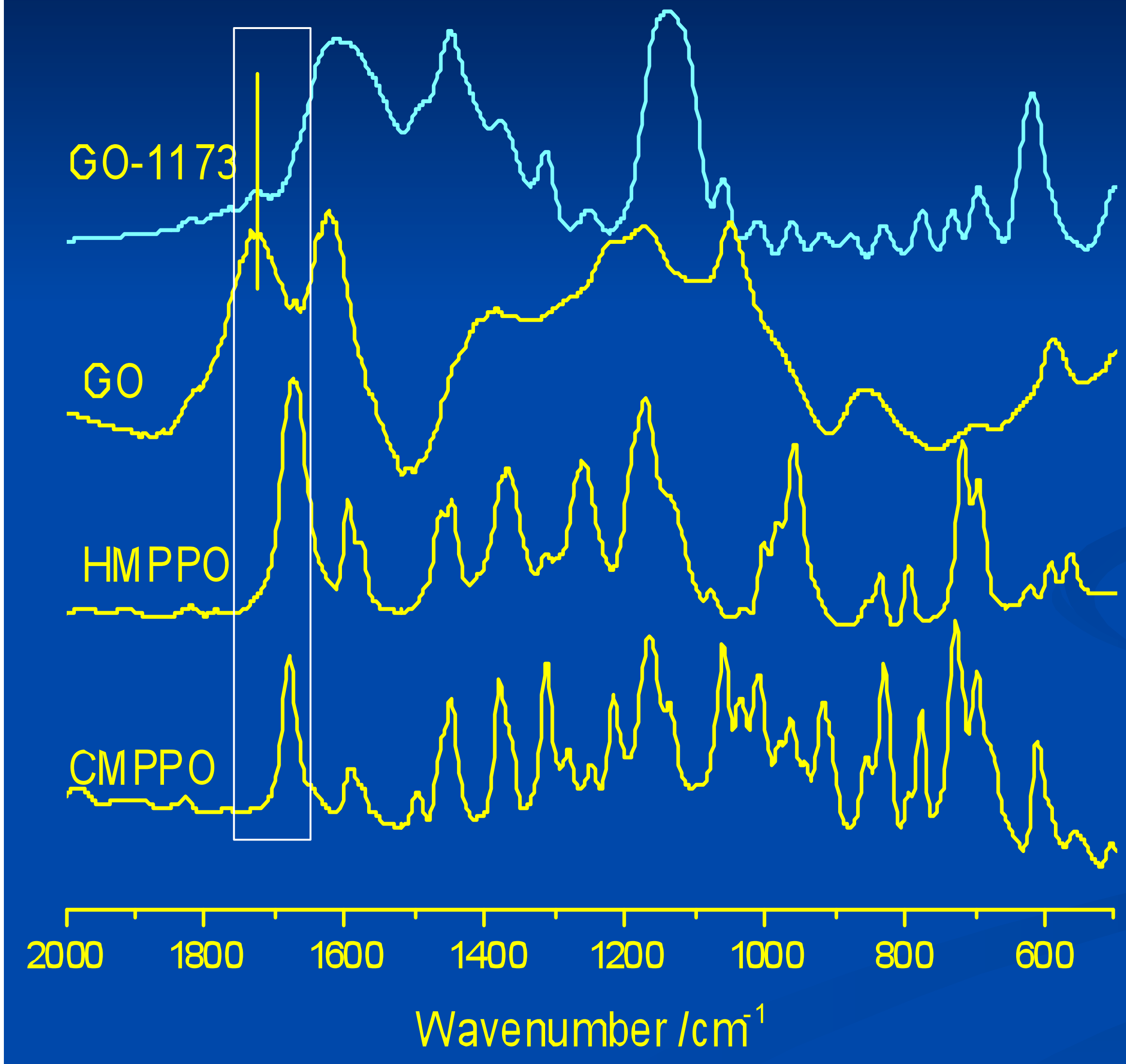


2-chloro-2-methyl-
1-phenylpropan-1-one (CMPPO)



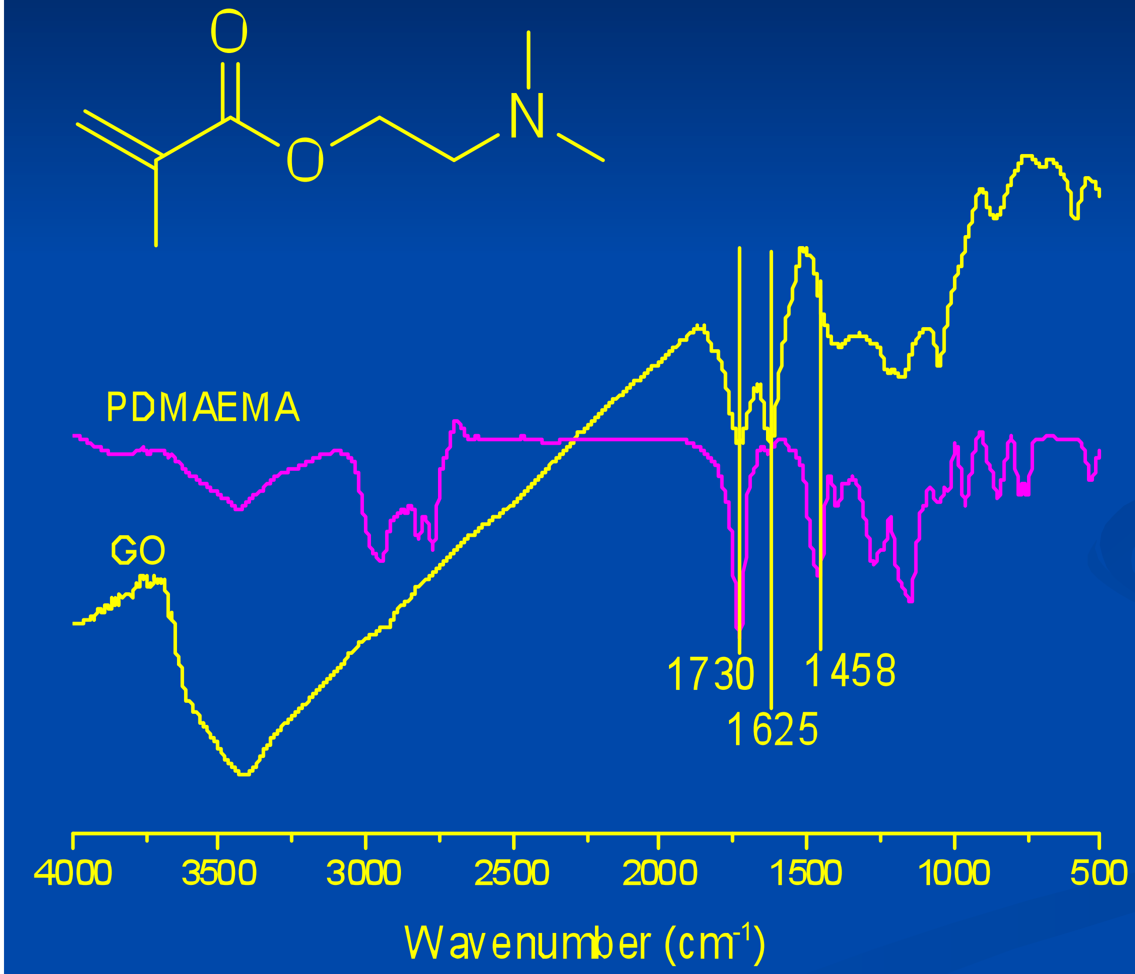
GO-1173

FTIR of immobilized photoinitiator



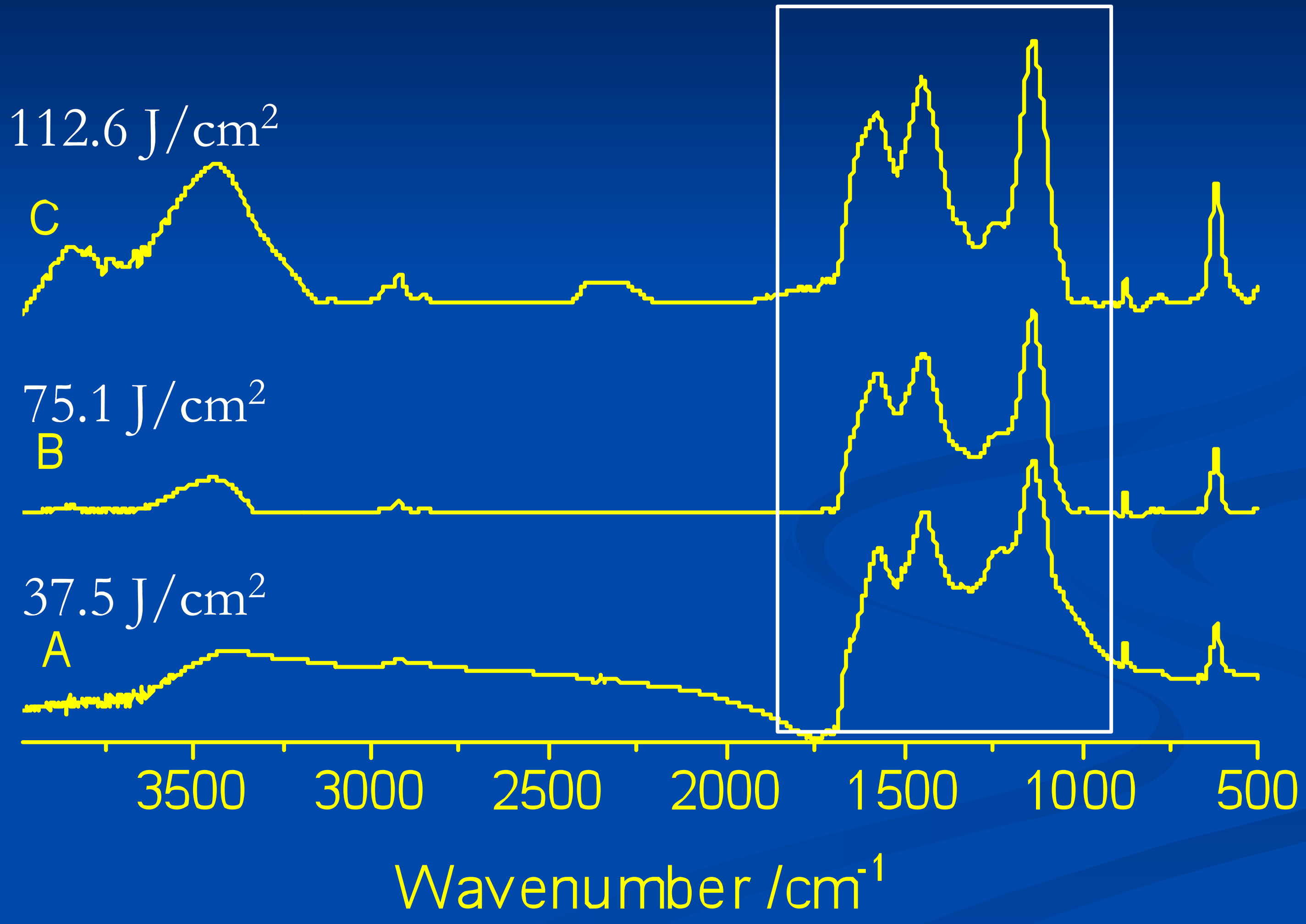
- After chemical modification, signals from surface carboxylic groups on GO disappeared.

FTIR of GO and PDMAEMA

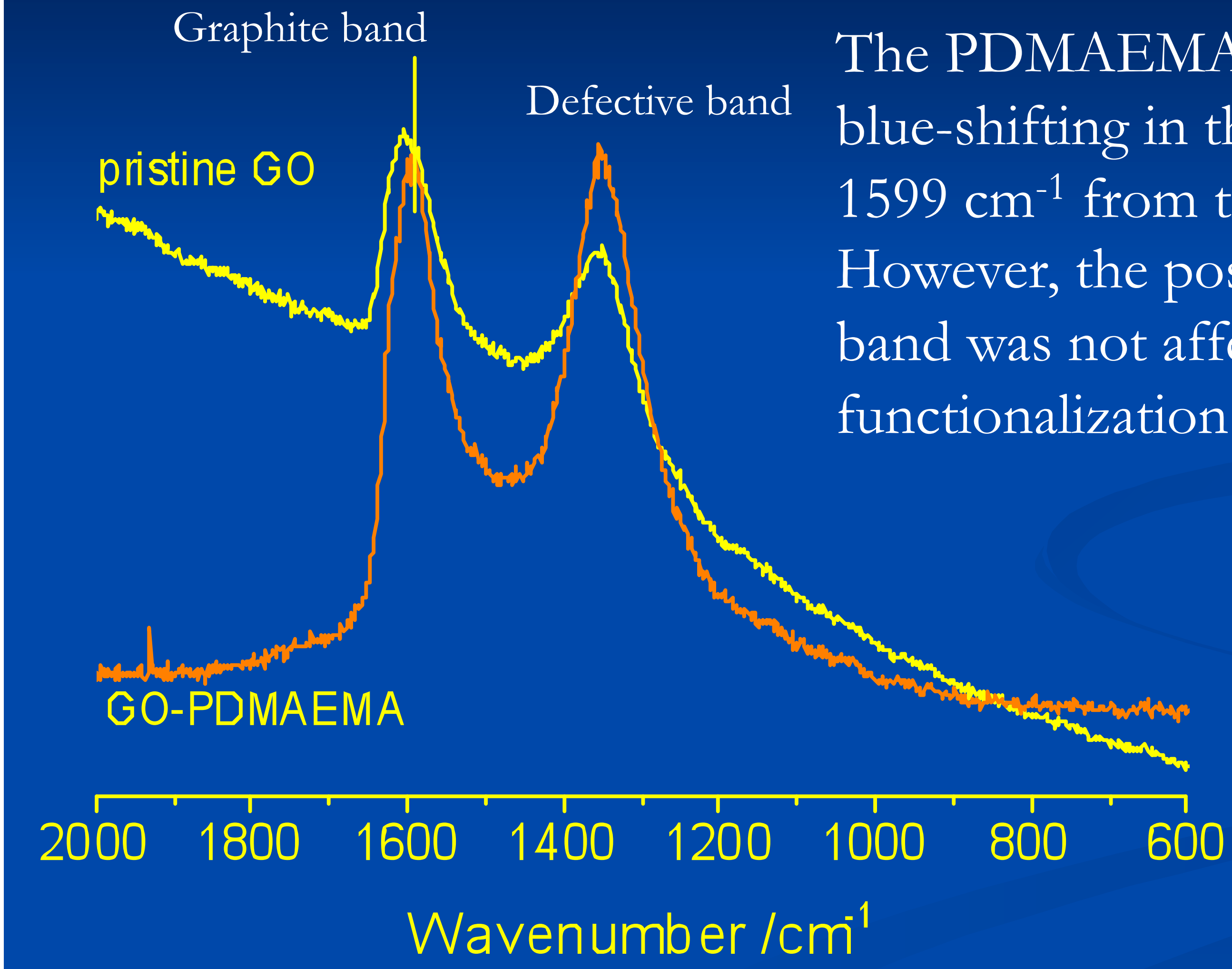


- 1730: stretching vibration of carbonyl group.
- 1458: deformation vibration of methyl group.
- 1625: stretching of aromatic skeleton.
- Ratio of peak at 1625 to that at 1730 – a measure of grafting degree

GO-1173/DMAEMA

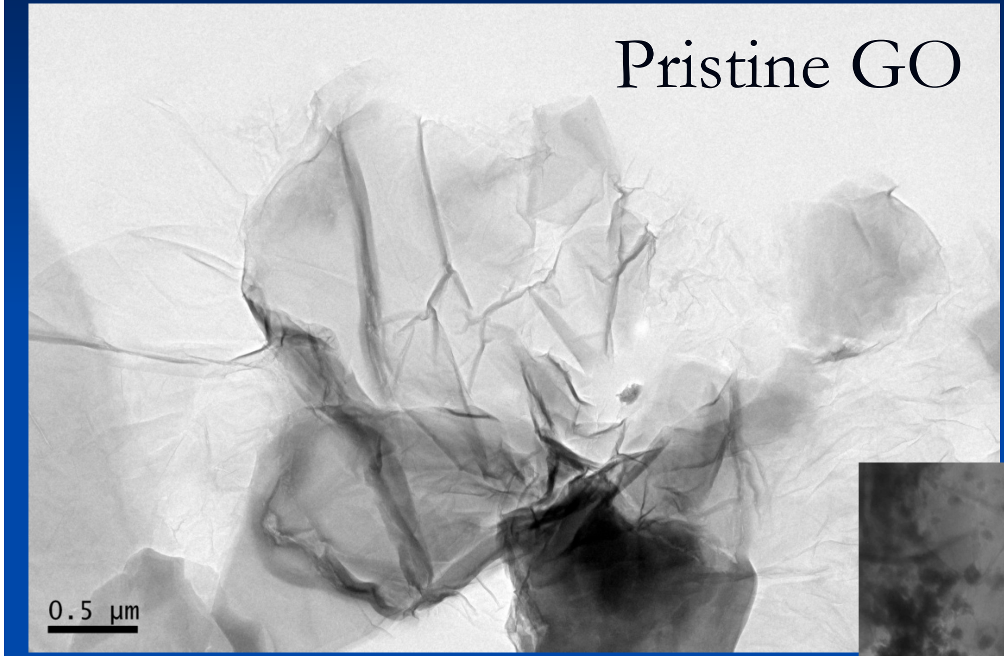


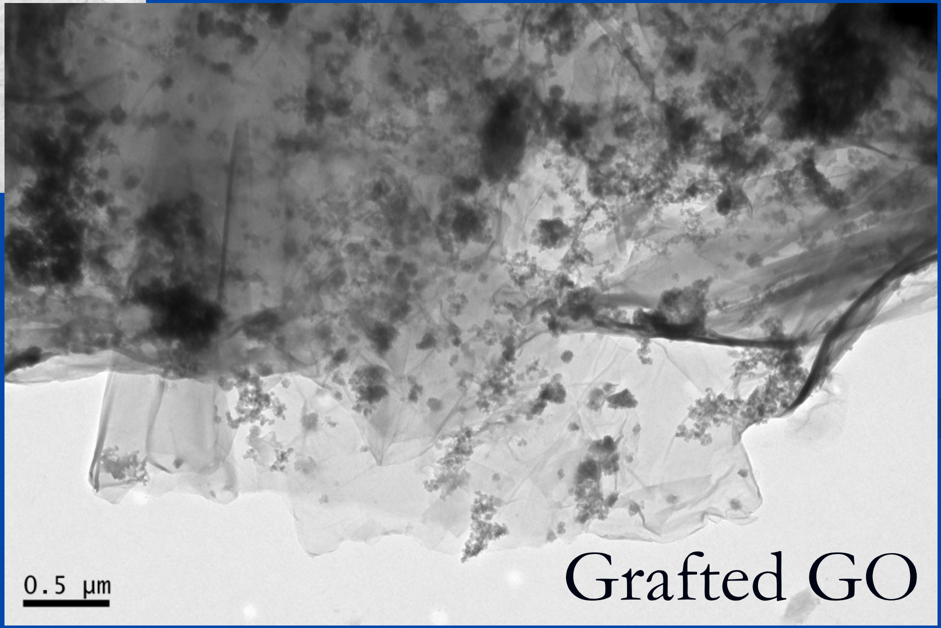
Raman of GO graft



The PDMAEMA grafted GO showed blue-shifting in the G band, moving to 1599 cm^{-1} from the original 1589 cm^{-1}. However, the position of the defective D band was not affected by chemical functionalization at all.

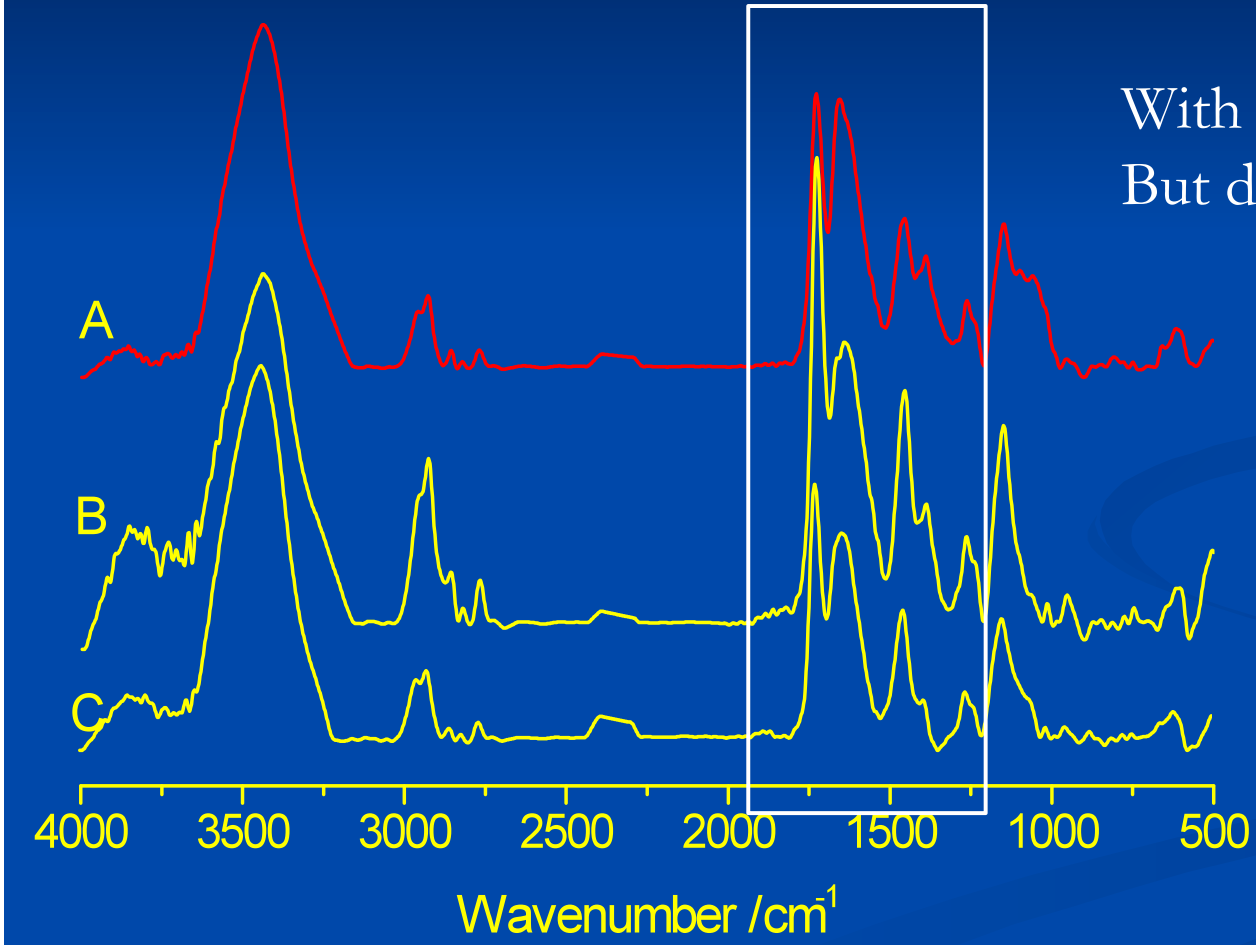
TEM of GO


Pristine GO


Grafted GO

Photoinitiated graft via dissolved initiator

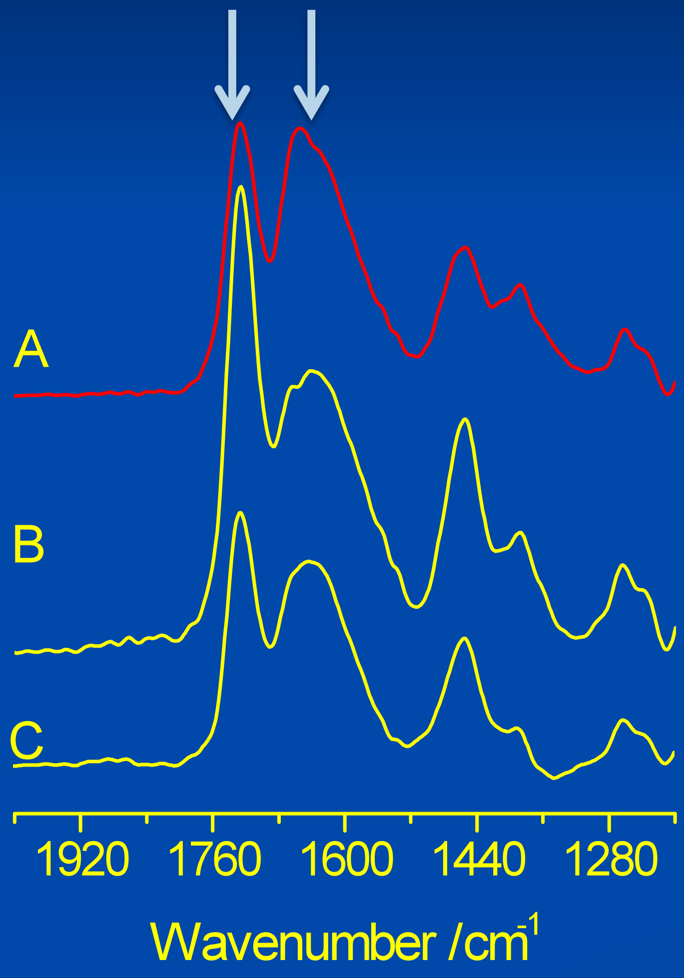
FTIR of GO-PDMAEMA obtained under different UV energy



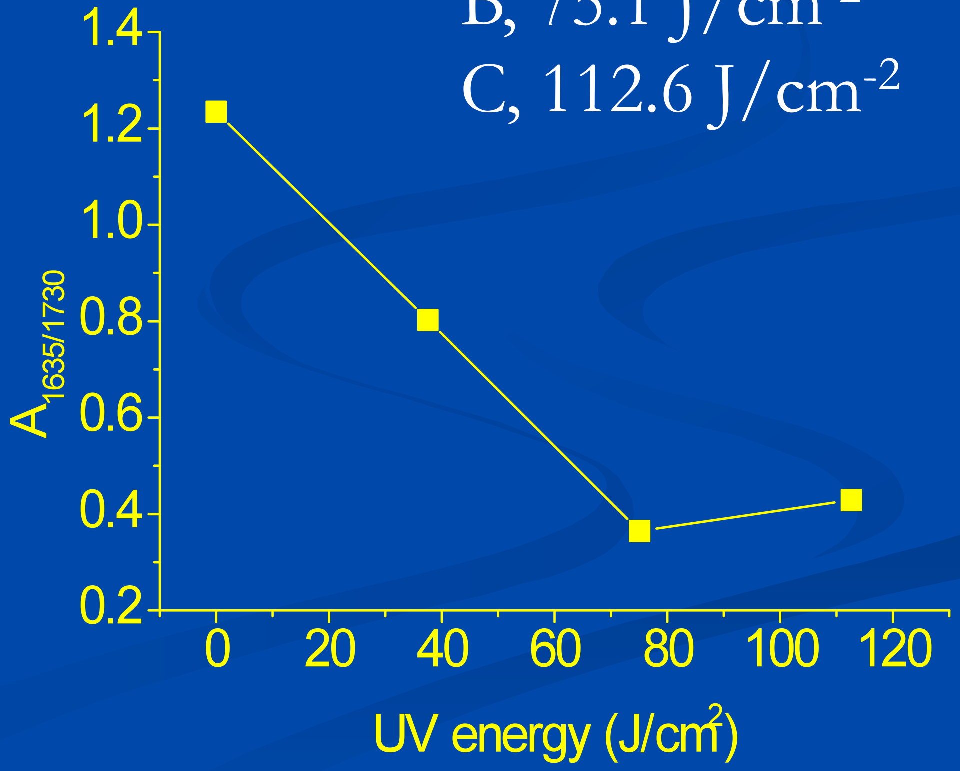
With same BPO concentration
But different photo exposure

A, 37.5 J/cm^{-2}
B, 75.1 J/cm^{-2}
C, 112.6 J/cm^{-2}

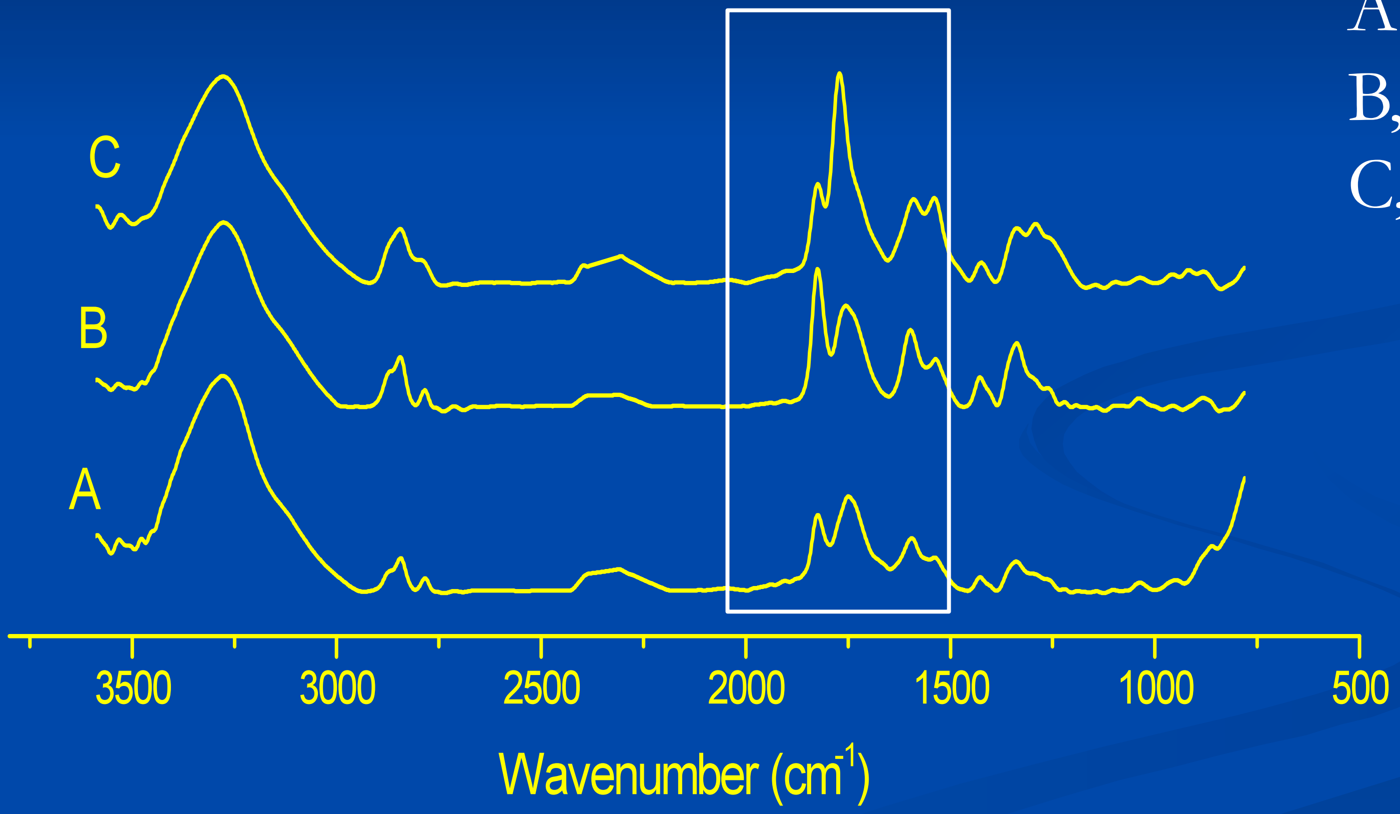
Relative intensity of peak at 1635 cm^{-1} to that of 1730 cm^{-1} decreases with increasing UV exposure, indicative of increasing graft.



A, 37.5 J/cm^{-2}
B, 75.1 J/cm^{-2}
C, 112.6 J/cm^{-2}



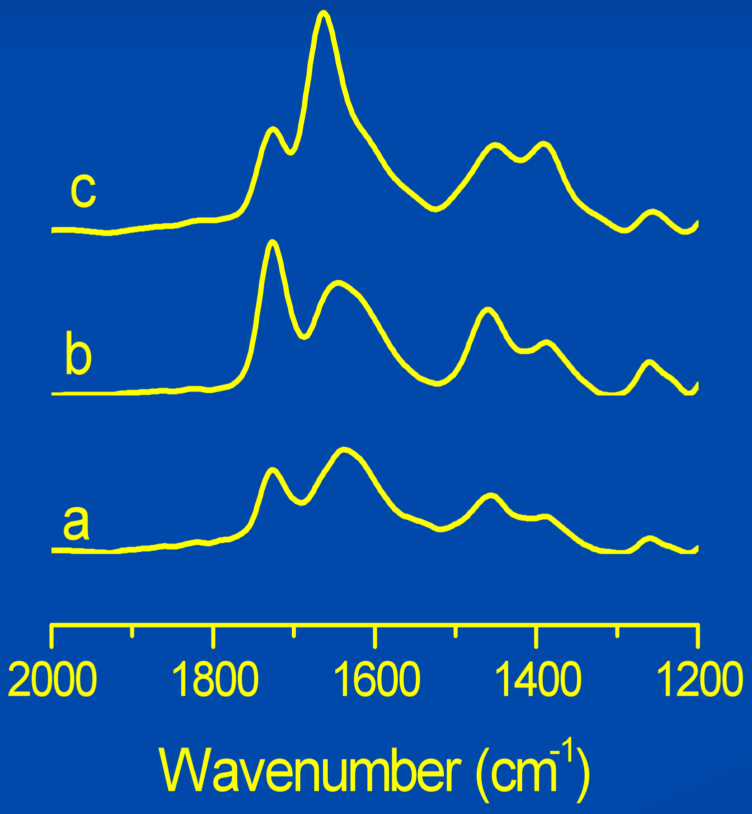
FTIR of GO-PDMAEMA obtained with different contents of BPO

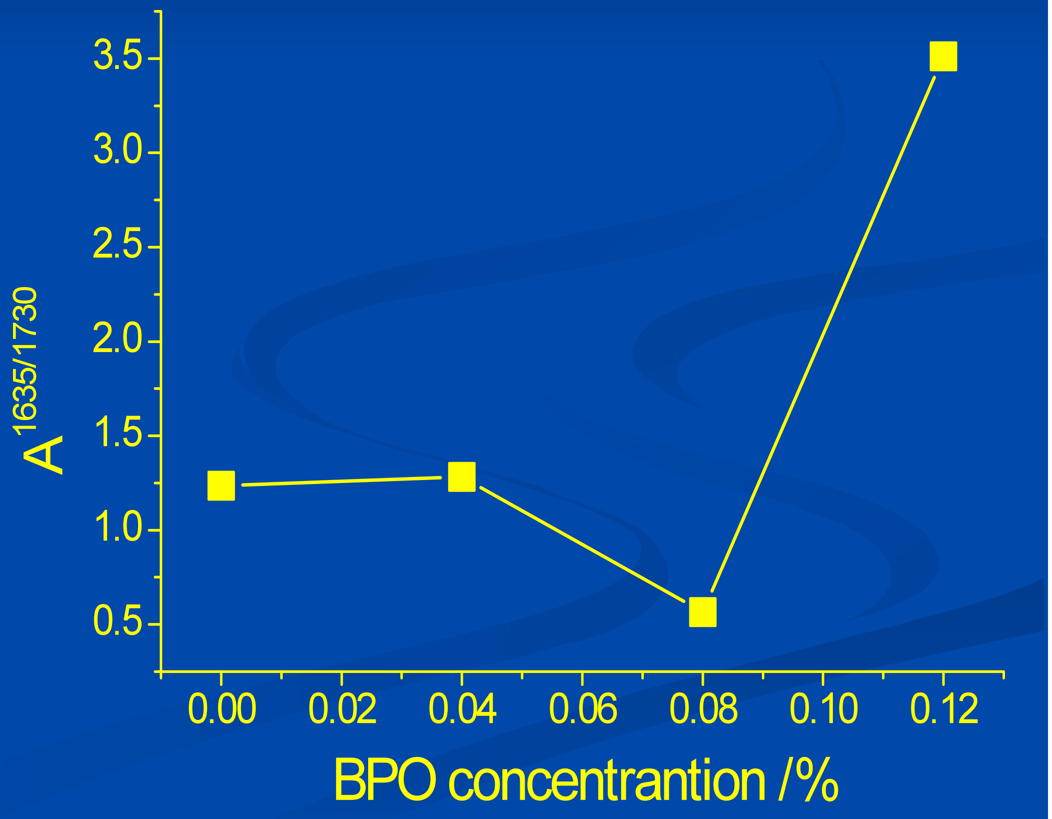


A, 4% BPO
B, 8% BPO
C, 12% BPO

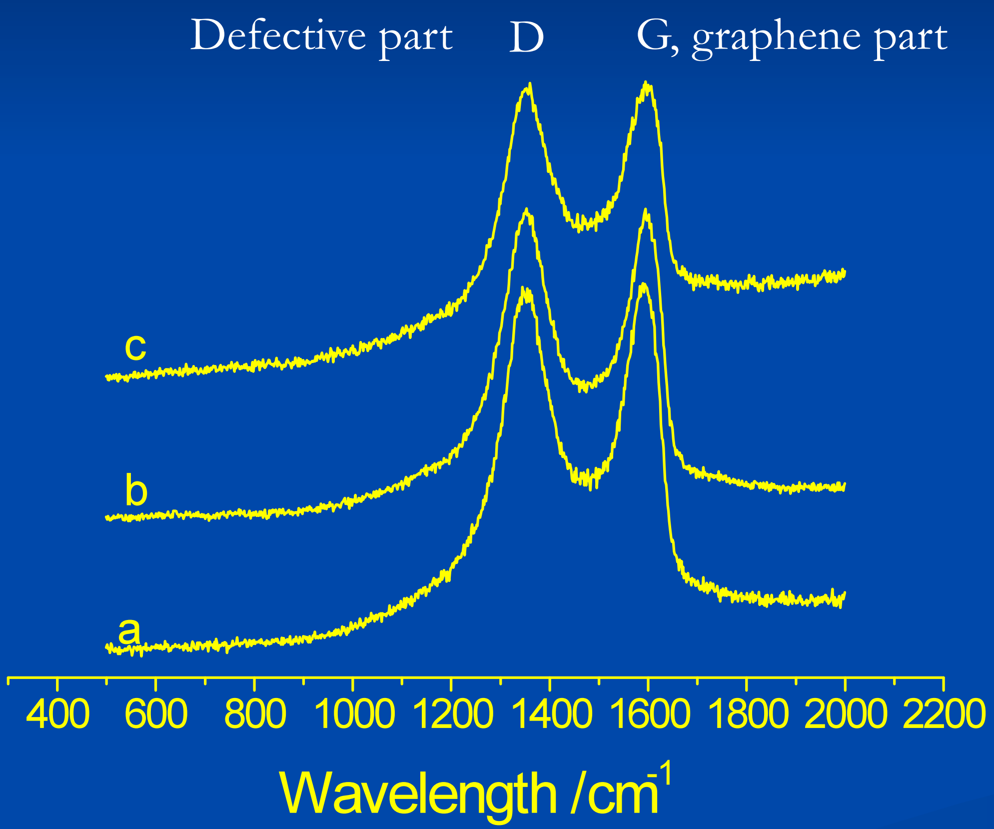
With increasing BPO concentration, Graft increases slightly, but decreases significantly, perhaps meaning that BPO is attached directly to GO.

A, 4% BPO
B, 8% BPO
C, 12% BPO





Raman of GO-PDMAEMA obtained at different BPO concentration



BPO, %	I_D/I_G
4%	1.18
8%	1.30
12%	1.39

Defective sites increase with more BPO initiator.

Grafting degree calculated according to elementary analysis

BPO, %wt	N%	Grafting, %wt
4	3.75	42.1
8	4.06	45.6
12	3.98	44.7

Molecular mass of homopolymers found in solutions

BPO	M_n	M_w/M_n
4%	7240	1.32
8%	5230	1.45
12%	3760	1.09

The molar mass of homopolymers found in solutions can be used to evaluate the graft length.

Conclusion

- Type II photoinitiator initiated graft of PDMAEMA onto GO was studied.
- Compared with photoinitiator immobilized on the surface of GO, photoinitiator dissolved in monomers seemed more efficiently to initiate grating polymerization, possibly because that the amount of initiator in the latter case was much higher than immobilized initiator.

Thank you for your attention!